PB85-221174

Exposure and Risk Assessment for Nickel

Little (Arthur D.), Inc., Cambridge, MA

Prepared for

Environmental Protection Agency, Washington, DC

Dec 81

U.S. Department of Commerce
National Technical Information Service
NTIS

50272-101

REPORT DOCUMENTATION PAGE

1. REPORT NO. EPA-440/4-85-012

2.

3. Recipient's Accession No. PB85 221174 /AS

4. Title and Subtitle

An Exposure and Risk Assessment for Nickel

5. Report Date Final Revision December 1981

6.

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8. Performing Organization Rept. No.

9. Performing Organization Name and Address

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10. Project/Task/Work Unit No. Task 3

11. Contract(C) or Grant(G) No.

(C) C-68-01-5949

(G) C-68-01-6017

12. Sponsoring Organization Name and Address

Monitoring and Data Support Division
Office of Water Regulations and Standards
U.S. Environmental Protection Agency
Washington, D.C. 20460

13. Type of Report & Period Covered Final

14.

15. Supplementary Notes

Extensive Bibliographies

16. Abstract (Limit: 200 words)

This report assesses the risk of exposure to nickel. This study is part of a program to identify the sources of and evaluate exposure to 129 priority pollutants. The analysis is based on available information from government, industry, and technical publications assembled in April of 1981.

The assessment includes an identification of releases to the environment during production, use, or disposal of the substance. In addition, the fate of nickel in the environment is considered; ambient levels to which various populations of humans and aquatic life are exposed are reported. Exposure levels are estimated and available data on toxicity are presented and interpreted. Information concerning all of these topics is combined in an assessment of the risks of exposure to nickel for various subpopulations.

17. Document Analysis a. Descriptors

Exposure
Risk
Water Pollution
Air Pollution
Effluents
Waste Disposal
Food Contamination
Toxic Diseases
Nickel

b. Identifiers/Open-Ended Terms

Pollutant Pathways
Risk Assessment

c. COSATI Field/Group 06F 06T

18. Availability Statement

Release to Public

19. Security Class (This Report) Unclassified

20. Security Class (This Page) Unclassified

21. No. of Pages 246

22. Price

(See ANSI-Z39.18) *See Instructions on Reverse* OPTIONAL FORM 272 (4-77)
(Formerly NTIS-35)
Department of Commerce

United States
Environmental Protection
Agency

Office of Water
Regulations and Standards (WH-553)
Washington DC 20460

December 1981
EPA-440/4-85-012

PB85-221174

Water

EPA

An Exposure and Risk Assessment for Nickel

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

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EPA-440/4-85-012
April 1981
(Revised December 1981)

AN EXPOSURE AND RISK ASSESSMENT FOR

NICKEL

by

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FOREWORD

Effective regulatory action for toxic chemicals requires an understanding of the human and environmental risks associated with the manufacture, use, and disposal of the chemical. Assessment of risk requires a scientific judgment about the probability of harm to the environment resulting from known or potential environmental concentrations. The risk assessment process integrates health effects data (e.g., carcinogenicity, teratogenicity) with information on exposure. The components of exposure include an evaluation of the sources of the chemical, exposure pathways, ambient levels, and an identification of exposed populations including humans and aquatic life.

This assessment was performed as part of a program to determine the environmental risks associated with current use and disposal patterns for 65 chemicals and classes of chemicals (expanded to 129 "priority pollutants") named in the 1977 Clean Water Act. It includes an assessment of risk for humans and aquatic life and is intended to serve as a technical basis for developing the most appropriate and effective strategy for mitigating these risks.

This document is a contractors' final report. It has been extensively reviewed by the individual contractors and by the EPA at several stages of completion. Each chapter of the draft was reviewed by members of the authoring contractor's senior technical staff (e.g., toxicologists, environmental scientists) who had not previously been directly involved in the work. These individuals were selected by management to be the technical peers of the chapter authors. The chapters were comprehensively checked for uniformity in quality and content by the contractor's editorial team, which also was responsible for the production of the final report. The contractor's senior project management subsequently reviewed the final report in its entirety.

At EPA a senior staff member was responsible for guiding the contractors, reviewing the manuscripts, and soliciting comments, where appropriate, from related programs within EPA (e.g., Office of Toxic Substances, Research and Development, Air Programs, Solid and Hazardous Waste, etc.). A complete draft was summarized by the assigned EPA staff member and reviewed for technical and policy implications with the Office Director (formerly the Deputy Assistant Administrator) of Water Regulations and Standards. Subsequent revisions were included in the final report.

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ACKNOWLEDGEMENTS

The Arthur D. Little, Inc., task manager for this study was Pamela Walker McNamara. Major contributors to this report were Melanie Byrne (Aquatic Effects and Exposure), Bruce Goodwin and Richard Thomas (Environmental Fate), Kate Scow (Biotic Fate and Risk), William Steber (Human Effects), and Melba Wood (Monitoring Data). In addition, Joseph Fiksel and John Ostlund assisted in the risk extrapolation and Krishna Aravamudan contributed to the discussion of atmospheric fate. Preparation of the final draft report involved Anne Littlefield (editing), Nina Green (documentation), Mary Ann Arvai (technical support), and Alfred Wechsler (technical review).

The materials balance for nickel (Chapter 3.0) was produced by Acurex Corporation under Contract 68-01-6017 to the Monitoring and Data Support Division (MDSD), Office of Water Regulations and Standards (OWRS), U.S. Environmental Protection Agency. Steve Wendt and Patricia Cruse were the task managers for Acurex Corporation.

Richard Healy and Richard Silver, MDSD, were the project managers at EPA.

1.0 TECHNICAL SUMMARY

This chapter is a summary of the evaluation of the risk associated with exposure to nickel. The risk is identified within the constraints of available data and the following subjects are also briefly discussed: adverse human effects and the levels at which they occur; exposure routes and levels; the principal environmental pathways; non-human risk, effects, and exposure; and the materials balance of nickel.

1.1 RISK TO HUMANS: EFFECTS, EXPOSURE, AND FATE CONSIDERATIONS

The risk associated with human exposure to nickel is minimal and is via inhalation of nickel carbonyl and nickel subsulfide. There is little risk associated with nickel ingested in drinking waters and dietary foods due to the high effects levels (443 µg Ni/kg body weight/day and greater in animal studies) and typically low exposure levels through ingestion--100 to 900 µg/day (1.4 to 12.9 µg Ni/kg body weight/day). Dermatitis can occur as a result of percutaneous (dermal) exposure to nickel, however, these effects are non-fatal.

Animal studies indicate that nickel carbonyl and nickel subsulfide are carcinogenic when inhaled; the respiratory tract and lungs are the principal target areas. Animal studies also indicate that nickel carbonyl is teratogenic and fetotoxic.

In this report, risk is evaluated in four exposure scenarios: ingestion of drinking water, inhalation of ambient air, inhalation of cigarette smoke, and dermal exposure.

There is little risk associated with ingestion of drinking water and food except on the rare occasion when nickel is present in water at concentrations significantly higher than 1 µg/l, a level commonly found in the environment. Abnormally high well water concentrations (maximum observed: 31,700 µg/l) which approached the effects levels observed in animal studies (443 µg Ni/kg body weight/day) were found on several brief occasions in the Ohio River Basin in 1978 and 1979.

Without speciation of reported ambient atmospheric nickel concentrations, the risk of inhalation of ambient air could not be evaluated.

A large portion of the nickel in tobacco is converted to nickel carbonyl during combustion. Making assumptions on smoking habits and brand of cigarette, the equivalent one-pack-a-day smoker is predicted to be at an excess lifetime per-captia risk of 0.05 to 0.1% due to the nickel carbonyl alone (excluding consideration of the other constituents of cigarette smoke).

Dermatitis due to percutaneous nickel contact is not fully understood but is not considered a life-threatening problem.

1.1.1 Effects Levels

The "background" level of exposure to nickel through ingestion, inhalation, and skin contact has not been shown to be particularly hazardous; on the other hand, certain nickel compounds, especially nickel carbonyl, are clearly toxic. Most nickel compounds are toxic only at elevated doses via routes of entry to the body that permit high concentrations of nickel to be achieved at the cellular or, more importantly, at the subcellular level.

The crucial consideration for assessing the risk of nickel toxicity is whether or not nickel can be absorbed and reach susceptible sites in the organism. This depends on the exposure route and the physicochemical form of the nickel. Nickel carbonyl is especially toxic because its combination of volatility, lipid solubility, and chemical stability permit rapid absorption by most routes into the organism, and subsequent wide extracellular and intracellular distribution. Intracellular decomposition and oxidation to Ni^{++} exposes sensitive subcellular processes to nickel ion. Thus, nickel carbonyl is a near ideal carrier for nickel, circumventing most of the protective mechanisms and barriers of the body. In contrast, orally ingested nickel salts have low toxicity because they are poorly absorbed and the absorbed portion is rapidly excreted from the body. High levels of nickel in the diet or drinking water of experimental animals are tolerated with minimal effects. The lowest ingested level of nickel found to cause adverse effects on neonates in animal studies was 443 μg Ni/kg body weight/day.

The major area of concern is toxicity from inhalation of nickel compounds. A number of studies and several recent reviews have indicated that nickel-refinery workers are at increased risk of developing respiratory tract cancer. The role of nickel in the development of respiratory tract cancer is not clear, however, because these workers were also co-exposed to other suspected carcinogens (e.g., asbestos and polycyclic aromatic hydrocarbons).

Animal studies indicate that nickel carbonyl and nickel subsulfide are carcinogenic by the inhalation route. These and some other nickel compounds cause adverse lung pathology and have been shown to alter lung "cleansing" processes, such as muco-ciliary clearance and alveolar macrophage activity. In vitro assays tend to support the in vivo carcinogenicity results for certain nickel compounds.

It has been reported that nickel carbonyl was found to be both teratogenic and fetotoxic in animal studies. Nickel contact dermititis is prevalent in humans but probably not life-threatening. Dermatitis has been an occupational problem in industries where exposure to nickel compounds is common. Non-occupational exposures causing nickel dermatitis have reportedly occurred following contact with clothing fasteners, jewelry, and dental alloys.

1.1.2 Exposure Levels

Nickel exposure through ingestion of drinking water does not appear to be a significant route due to the generally low concentrations of the metal found in well waters and treated drinking water systems. Except in rare instances, drinking water concentrations were below the established Human Health Water Quality Criterion of 13.4 μg/l. Oral intake of nickel in the human diet (including drinking water) typically contributes 100 to 900 μg/day to the body. Little is known about the chemical form of nickel in foods, however, nickel in water is poorly absorbed and it is believed that nickel in many foods is also poorly absorbed.

Nickel in ambient air occurs in fairly low concentrations ranging from 0.6 ng/m^3 to 690 ng/m^3 and typically at 6 ng/m^3 in non-urban air and about twice as concentrated in urban air. In areas near intense industrial activity with associated high nickel emissions, the nickel concentrations are higher but speciation is unknown. Cigarette smoking may contribute 15 μg/day of nickel carbonyl to the average one-pack-a-day smoker.

Percutaneous exposure occurs as a result of contact with nickel-bearing objects (e.g., stainless steel kitchenware, jewelry, dental alloys). Upon contact with such objects, the skin of some individuals may become sensitized, however more study is needed on the grade of alloy from which these objects are made and the associated releases of nickel.

In order to fully evaluate nickel exposure, its chemical form in different exposure scenarios must be identified. The most serious effects to humans are caused by inhalation of nickel carbonyl and nickel subsulfide, and the available data provide exposures to ambient levels of unspecified nickel. Nickel speciation in critical exposure areas has not been sufficiently evaluated to determine exposure.

1.1.3 Environmental Fate of Nickel and Associated High Exposure Levels

Nickel is the 24th most abundant mineral on the earth, and as a result of erosion and other physically, chemically, and biologically degrading processes nickel occurs in all of the environmental media in low background concentrations. Elevated concentrations of nickel appear to be fairly restricted to localized areas which are associated with industrial activity and the urban environment.

Nickel is typically found in low concentrations in ambient surface waters, well waters, and in other community drinking water supplies. Typical ambient and well waters contain nickel in the range of 5 to 10 μg/l and industrial and municipal waters have an average nickel concentration of 47 μg/l.

The air is a significant initial pathway because of its large portion of associated releases and because it is an important transport mechanism. Areas in the vicinity of high atmospheric releases of nickel are likely to experience high nickel concentrations in the surrounding soil, water, and vegetation. There are a number of industrial and urban-related activities utilizing nickel-bearing materials which account for much of the atmospheric release in populated areas.

Fossil fuels are possibly the most significant consumed products throughout the United States which contain nickel and consequently release large quantities of nickel to the atmosphere. The activities associated with the use of petroleum and coal (including production, refining, combustion) directly and indirectly affect the nickel concentration in all of the environmental media through processes such as dry deposition, runoff, and plant uptake. It is in locations where these activities are intensified that the nickel concentrations become elevated.

Nickel, a natural soil constituent, enters the food chain through plant uptake; elevated concentrations can be found in sludge-amended crops. Highest concentrations are found in leafy vegetables. Food contamination also results from air releases of nickel associated with industrial activity. Potential industrial sources of these residuals include dry deposition in the vicinity of nickel smelters.

A large amount of nickel is land disposed each year by industries and in municipal sludge. Horizontal migration through the soil is generally low and, except in direct application of sludge to crops or in the reuse by farming of old disposal areas, land-disposed nickel generally has not caused elevated concentrations of the metal in plants. Vertical migration of land-disposed nickel to groundwaters has not been found.

The contamination of aquatic species which humans consume is difficult to evaluate for several reasons. Generally, the nickel concentration in water and its availability (associated with pH, hardness) are low, and ingestion of nickel by fish is also low. An exception would be in isolated instances of abnormally high nickel concentration in ambient waters, such as was reported to the STORET Water Quality System on several occasions over the past 10 years in parts of Pennsylvania, West Virginia, Ohio, and Illinois.

1.2 RISK TO NON-HUMAN BIOTA

Aquatic species exposed to nickel in ambient waters are at low risk. Exposure typically occurs in isolated locations for short periods of time. Chronic effects levels have been reported for fish living in soft freshwater at nickel concentrations of 2 mg/l or greater. Invertebrates have been found to be more sensitive to nickel, experiencing effects at 0.5

mg/l or greater. Little data are available on salt water species, although they are believed to be less sensitive than freshwater organisms to nickel exposure. Freshwater algal species have experienced adverse effects at far lower nickel concentrations (1 to 10 μg/l) which are commonly found in ambient waters.

Nickel concentrations in ambient waters are typically below the 0.5 mg/l to 2 mg/l levels which have been identified as causing effects. Over the past 10 years, the STORET Water Quality System has reported elevated concentrations in the range of effects levels on rare occasions. These were in isolated locations (primarily the heavily industrialized Ohio River Basin) for brief periods of time.

The non-human risk suggested is further modified by the assumption that the exposure concentrations of nickel are totally available for aquatic organism absorption. This assumption is an unreasonable one and additional local characteristics (e.g., pH, hardness) must be further analyzed.

1.3 MATERIALS BALANCE

The largest portion of all identified environmental releases of nickel is to land (20,710 kkg or 63%) followed by air (10,030 kkg or 30%) and aquatic discharges (2350 kkg or 7%).

Of the aquatically discharged nickel, 1810 kkg are discharged directly to surface water and 540 kkg are discharged to POTWs. Close to 60% of the direct discharges are from the ferrous and nonferrous (iron and steel) smelting and refining industries. Primary and secondary production and recovery of nickel accounts for 30% of the direct aquatic discharges. Of the remaining 10% of direct aquatic releases, most is contributed as a result of utilization of fossil fuels; electroplating and production of chemical catalysts and batteries produce less than 3% of the aquatic discharges.

Only 8% to 11% of the estimated 4860 kkg to 6500 kkg of nickel released each year by POTWs is accounted for in influent from indirect dischargers to POTWs. Slightly more than half of the identified contribution to POTWs is from recovery of new and old scrap. An estimated 28% is discharged by the electroplating industry and 18% by ferrous smelting and refining, with the remainder from production of chemical catalysts and batteries. The remaining 89 to 92% may be discharged to POTWs as a result of urban runoff (unquantified), unidentified inadvertent releases associated with man, and natural sources. In the studies that have been conducted, POTWs have not removed nickel from treatment streams in consistent quantities.

Almost 89% of all atmospheric releases of nickel are from combustion of fossil fuels. Nickel occurs as a trace element in coal and petroleum products and consequently is released as a result of fuel combustion for power generation, space heating, and vehicular use. Alloys manufacturing accounts for 5% of nickel releases to air and the manufacture of cement for 4%. The remainder is accounted for by primary and secondary production and recovery, ferrous smelting and refining, and battery production.

Land receives the largest environmental release with contributions from production processes, uses, and inadvertent sources. As with releases to air, utilization of fossil fuels is the largest source (34%) of land-disposed nickel. The manufacture of cement is the second largest source of nickel to land (26%), followed by primary and secondary production (16%), electroplating (15%), and ferrous and nonferrous smelting and refining (9%). Other identified releases are small (less than 4 kkg) and include chemical and catalyst manufacturing, battery manufacturing, and tobacco processing.

2.0 INTRODUCTION

The Office of Water Regulations and Standards (OWRS), Monitoring and Data Support Division, U.S. Environmental Protection Agency is conducting a program to evaluate the exposure to and risk of 129 priority pollutants in the nation's environment. The risks to be evaluated include potential harm to human beings and deleterious effects on fish and other biota. The goal of the task under which this report has been prepared is to integrate information on cultural and environmental flows of specific priority pollutants and to estimate the risk based on receptor exposure to these substances. The results are intended to serve as a basis for developing suitable regulatory strategy for reducing the risk, if such action is indicated.

This report is intended to provide a brief, but comprehensive, summary of the production, use, distribution, fate, effects, exposure, and potential risks of nickel. Waterborne routes of exposure are stressed due to the emphasis of the OWRS on aquatic and water-related pathways.

The major problem associated with evaluation of nickel risk arises from the lack of identified speciation of levels known to occur in the environment. Significant adverse effects of inhalation exposure occur because of nickel compounds in air, however monitoring data only reports total nickel. Ingestion exposure of nickel in water and in the diet does occur, but in the case of dietary foods it is difficult to assess the risk because of a lack of information on the chemical form of nickel in foods.

Within the limits of existing data, exposures were evaluated for nickel ingestion in drinking water and food, inhalation of ambient air, inhalation of cigarette smoke, and percutaneous (dermal) exposure. These exposures consider the availability of nickel salts, nickel carbonyl, and nickel subsulfide and, in the absence of better information, utilize existing monitoring data on total nickel (nickel ion and compounds).

This report is organized as follows:

- Chapter 3.0 covers materials balance and contains information on releases from the production, use, and disposal of nickel including identification of the form and amounts released and the point of entry into the environment.
- Chapter 4.0 considers the fate of nickel leading from the point of entry into the environment to exposure of receiving and transporting medium. Reports of available data regarding concentrations detected in environmental media are also discussed.

- Chapter 5.0 discusses the adverse effects of nickel and several compounds, identifies concentrations eliciting these effects in humans, uses various techniques to extrapolate dose-response data, and quantifies the likely pathways and levels of human exposure.

- Chapter 6.0 considers the effects of nickel on biota and quantifies the environmental exposure of aquatic biota to nickel compounds.

- Chapter 7.0 discusses risk considerations for various subpopulations of humans and aquatic organisms.

- Appendices A, B, and C present the assumptions and calculations for the estimated environmental releases of nickel described in Chapter 3.0. Appendix D presents the assumptions and calculations for atmospheric fate in Chapter 4.0. Appendix E contains a listing of the STORET system's major river basins.

3.0 MATERIALS BALANCE

3.1 INTRODUCTION

In 1979, approximately 75% of the nickel used in the United States was imported, 5% was contributed by a domestic mine, 14% came from the refining of imported matte, and 6% stemmed from secondary production. The majority of the nickel domestically consumed for that year was used in alloys, followed by electroplating, battery production, and chemicals/catalysts. Salient statistics on the production (direct and indirect) and use of nickel are listed in Table 3-1 and Figure C-1, Appendix C.

Table 3-1 and Figure C-1 also show the quantities of nickel released to each environmental compartment from its production, use, and inadvertent sources. Approximately 30% of these wastes were atmospheric, 10% aquatic, and 60% terrestrial. The largest source of nickel wastes emitted to the atmosphere was the combustion of fossil fuels (8990 kkg), especially from coal burned by power plants. Two other major sources of atmospheric nickel releases were the manufacture of nickel-containing alloys (340 kkg), especially heat resistant stainless steels, and cement manufacture (407 kkg).

Nearly 2350 kkg of nickel were discharged to water in 1979. Approximately 1810 kkg and 540 kkg were released directly to surface waters and indirectly to surface waters through POTWs, respectively. The largest source, ferrous metal (iron and steel) smelters/refineries, discharged 1164 kkg or 50% of the total nickel released to the aquatic environment. The other major sources of aquatic nickel releases were secondary nickel production (688 kkg), electroplating (200 kkg), fossil fuel combustion (150 kkg), and a U.S. nickel refinery (132 kkg).

Most of the 20,710 kkg of nickel disposed as waste to land came from the combustion of fossil fuels (7030 kkg) and cement manufacture (5370 kkg). The other major contributors were electroplaters (3040 kkg), a domestic nickel mine (2600 kkg), various industrial processes (1958 kkg), and secondary nickel producers (570 kkg).

3.2 NATURAL BACKGROUND LEVELS OF NICKEL

Not all the nickel found in the environment comes from manmade sources. Nickel also occurs naturally where an estimated 0.008% is found in the earth's crust. Nickel occurs in rocks and soils largely as a component of sulfide, silicate, oxide minerals, and humus complexes. Nickel exists as Ni^{++} or as colloidal complexes in natural waters and as a trace element in living organisms. Furthermore, nickel is found in the atmosphere where it is usually associated with aerosols or particulates. Selected physical and chemical properties of nickel and its complexes are shown in Tables C-1 and C-2, Appendix C.

Table 3-1. Materials Balance: Nickel, 1979 (kkg)

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			Estimated Wastes (kkg)					
				Water[c]				
Source	Input[a]	Contained[b]	Air	(T)	(S)	POTW	Land	Total
Production and Recovery								
Primary								
Hanna Operations[d]								
Mining/Milling	1,285,000[e]	12,300[f]	neg[g]	1[h]	1[h]		2,600[i]	2,600
Smelting		10,600[j]	neg[g]	1[h]	1[h]		neg[k]	1
AMAX Operations[l]								
Smelting/Refining		29,300	30[m]	132[m]	132		132[m]	295
Secondary (scrap)								
Nonferrous Metal								
New Scrap: Ni-base		2,300	2[m]	10[m]	10[m]		10[m]	23
Cu-base		2,800	2[n]	565[o]	327[o]	137[o]	464[o]	1,031
Al-base		1,700	neg[p]	neg[p]			neg[p]	neg
Old Scrap: Ni-base		4,600	5[m]	21[m]	21[m]		21[m]	47
Cu-base		440	1[n]	92[o]	53[o]	38[o]	75[o]	168
Al-base		160	neg[p]	neg[p]			neg[p]	neg
Coproduct and By-Product Nickel (Copper Industry)		5	neg[r]	neg[r]			neg[r]	neg
Inadvertent Sources								
Fossil Fuels	16,230	16,230	9,990[s]	150[s]	150[s]		7,130[s]	16,170
Cement Manufacture			403[w]	neg[w]			5,370[w]	5,773
Asbestos Manufacture			neg[x]	neg[x]			neg[x]	neg
Tobacco			neg[y]	neg[y]			1[y]	1
Use								
Industrial Processes								
Ferrous Smelting/Refining[u]		40,200[t]	52[u]	1,164[v]	1,068	98	1,262[v]	2,478
Nonferrous Smelting/Refining								
Primary			neg[v]	neg[v]			536[v]	536
Secondary			neg[v]	neg[v]			164[v]	164
Alloys:								
Stainless Steel Heat Resistant Steel	67,670	67,330	340[z]	neg[aa]			neg[aa]	340
Other Steel Alloys	19,370	18,975	95[z]	neg[aa]			neg[aa]	95
Supper Alloys	15,400	15,385	15[z]	neg[aa]			neg[aa]	15
Nickel-Copper & Copper-Nickel Alloys	9,790	9,780	10[z]	neg[aa]			neg[aa]	10
Permanent Magnet Alloys	730	729	1[z]	neg[aa]			neg[aa]	1
Other Nickel Alloys	41,130	41,059	40[z]	neg[aa]			neg[aa]	40
Cast Iron	3,240	3,210	30[bb]	neg[aa]			neg[aa]	30
Electroplating	27,500	23,500	neg[cc]	200[dd]	50[dd]	150[dd]	3,040[ee]	3,240
Chemicals/Catalysts	1,060	1,049	neg	3[ff]	2[ff]	2[ff]	4[ff]	7
Batteries	1,470	1,450	6[gg]	14[hh]	1[hh]	13[hh]	3[ii]	23
Total			10,030	2,350	1,810	540	20,710	33,090

Footnotes next page

Table 3-1. (Continued)

a) Totals may not add due to rounding.
b) Sibley, 1980.
c) T = total; S + POTW = T, where S = surface water and POTW = Publicly Owned Treatment works.
d) See Note 1, Appendix A for description of Hanna operations.
e) Total nickel-containing ore.
f) Ferronickel recovered.
g) Negligible, (<1 kkg); aerosols are not readily formed due to high moisture content of mineral, Matthews, 1979.
h) EPA, 1975b; see Appendix A, Note 2 for further details.
i) Based on plant estimates of 17% of total mined ore is discarded, Boldt, 1967; 1.2% nickel contained in ore, Matthews, 1979.
j) Total ferronickel shipped from production site; 2,200 kkg of ferronickel was stockpiled, Sibley, 1980.
k) Slag is granulated and metal values recovered and charged to refining furnaces, Boldt, 1967.
l) See Note 3, Appendix A and Figure C-2, Appendix C for description of Amax operations.
m) Approximately 1% of nickel input lost during processing, Hoppe, 1977; assuming 1 kg nickel emitted to air per kkg nickel produced, EPA 1973b, the remaining wastes equally divided between water and land.
n) Approximately 1 kg nickel emitted to air per kkg nickel charged, EPA, 1973b.
o) Based upon difference in amount of nickel in treated and untreated discharges; nickel removed during treatment is disposed to land; see Appendix A, Note 5 for further details.
p) Wastes <1 kkg nickel considered negligible, see Table 3-5 for calculations; EPA, 1979a.
q) Confidential company data, Sibley, 1980.
r) Less than 1 kkg of nickel assumed to be produced, see Appendix A, Note 6 for details.
s) Slater and Hall, 1977. See text, Table C-7, Appendix C and Appendix A, Note 7 for details.
t) To include ferroalloys
u) Copeland, 1980; see Appendix A, Note 4 for calculation.
v) See Table 3-7 for details.
w See Table C-10, Appendix C for details.
x) Less than 1 kkg nickel emitted to the atmosphere and no other wastes were generated due to nickel's affinity for the asbestos mineral (Wood,1980; Clifton, 1980).
y) Department of Agriculture, 1979. EPA, 1978b; see text for further details.
z) Based on 5 kg of nickel emitted to air per metric ton of nickel charged, EPA, 1973b.

Table 3-1. (Concluded)

aa) Assumed to be <1 kkg because water used in alloy production is noncontact cooling water and scrap metal is recycled within plant, Matthews, 1979.
bb) Based on 10 kg nickel emitted to air per kkg nickel charged (assuming no control), EPA, 1973b.
cc) Air sparging of plating solution tanks yields negligible quantities of nickel, EPA, 1973a; Masarik, 1980.
dd Based on annual discharges of 0.45 kkg per plant and 433 plants; see Appendix A, Note 8 for details.
ee) Based on 95% of nickel in wastewater was contained in sludge, Patterson, 1976; Masarik, 1980; and 200 kkg remained in water after treatment; see Appendix A, Note 8 for details.
ff) See Appendix A, Note 9. Assume discharges to be equally divided between surface and POTWs waters.
gg) Based on an uncontrolled emission estimate of 4 kg nickel emitted to the atmosphere per kkg of nickel processed as batteries, EPA 1973b.
hh) See Appendix A, Note 10.
ii) To include primary and secondary scrap.

3.2.1 Nickel in Minerals and Soils

Nickel exists in many forms when contained in rocks and soils (Schroeder et al. 1962, Bowen 1966, Underwood 1971). The chief minerals of nickel found in the environment are shown in Table C-3, Appendix C. Native nickel in a near or absolutely pure form is unknown.

There are two principal classes of nickel ore: oxide (silicate) deposits and sulfide deposits (Adamec and Kihloren 1968). Oxide ores (laiterites) are a product of chemical action by weathering of rocks which are high in magnesium and iron but low in nickel content. These are the ores mined in the United States. In the silicate type of oxide ore, nickel is found in the lattice of hydrated magnesium-iron minerals such as garnierite. Approximately 1-3% nickel is found in the widely distributed ores. In the sulfide ores, nickel is found mainly as the mineral pentlandite, which contains approximately 0.1-3% Ni, 0.2-3% Cu, 5-25% S, and 10-35% Fe, with the remainder composed of refractory oxides (Adamec and Kihloren 1968).

Rocks in the upper part of the earth's crust supply most of the minerals from which soils are formed, via weathering, and thus are a major source of nickel in soils. The National Academy of Sciences reports that nickel concentrations in soils generally range from 5-500 mg/kg; the concentration in U.S. soils averages 30 mg/kg (NAS 1975). Other sources indicate that nickel is found at average concentrations of 50 mg/kg in sedimentary rocks, shale, and carbonate rocks (see Section 4.5 - Monitoring Data).

3.2.2 Nickel in Aquatic Systems

Upon weathering, nickel contained in minerals is transformed into the insoluble minerals of hydrolysates. This means any nickel contained in surface waters or groundwaters is likely to be present only in small amounts, unless due to manmade pollution (NAS 1975, Koop and Kroner 1970). (For additional data see Section 4.5 - Monitoring Data).

3.2.3 Nickel in the Atmosphere

Generation (and removal) of aerosols occurs by a variety of mechanisms, including sea surface-to-air transport, gas-to-particle conversion, wind erosion, man's activities, volcanic activity, forest fires, descent of meteoric debris, and plant exudation (Mulvey 1979). The relative aerosol production rates of most of these processes are shown in Table C-5, Appendix C.

The sea surface-transport mechanism appears to contribute approximately 40 kkg of nickel to the air (see Note 11, Appendix A, for further details). Nriagu (1979) estimated the quantity of nickel emitted per year from worldwide volcanic activity to be nearly 3800 kkg (see Note 12, Appendix A, for further details). Estimated aerial fallout of nickel to a 10,000-km area from a forest fire was 120 kg/day (Young and Jan 1977) (see Note 13, Appendix A, for further details). Data regarding nickel emissions from meteoric debris fallout are unavailable but the emissions may be significant due to the high nickel content of meteorites. Finally, 200 kkg of nickel are assumed to be released from plant exudations (see Note 14, Appendix A, for further details).

3.3 MANMADE SOURCES OF NICKEL

Approximately 30% of the nickel consumed in the United States during 1979 was produced domestically; the remaining 70% was imported (Sibley 1980). The largest single U.S. resource is found in the form of low-grade Duluth gabbro of northeastern Minnesota. The second largest U.S. nickel deposit, composed primarily of nickel silicates and oxides, is found in southern Oregon and northern California--the site of the only U.S. nickel mine and smelter for domestic ores (i.e., Hanna Mining Company, Riddle, Oregon; see Note 1, Appendix A, for further details).

Nickel imported into the United States for refining is in the form of nickel-copper-cobalt matte. The matte is processed by the AMAX Nickel Division located at Port Nickel, Louisiana (see Note 3, Appendix A, for further details). Table 3-2 lists the quantity (and percent) of nickel produced in the United States for 1979.

3.3.1 Mining, Milling, and Smelting of Nickel-Containing Ores

The Hanna Mining Company, which operates an open pit mine, provided 10,600 kkg of nickel (less 2200 kkg stockpiled by Hanna) or 20% of the total nickel produced in the United States in 1979.

In the production of ferronickel, various wastes which contain nickel are also produced (e.g., rejected submarginal ore, residual rock, mine area runoff, process wastewater, and aerosols). Of the estimated 1,285,000 kkg of ore mined in 1979 (Table 3-2), 17% (218,450 kkg) was rejected at the screening plant (Boldt 1967). However, it is unlikely that significant amounts of nickel leached from this ore (via weathering) because (1) its nickel content was <1.2% (Matthews 1979) and (2) nickel leaches from ore at a very slow rate. Atmospheric emissions of nickel from mining (as ore dusts) appear to be minimal because dusts generated during mining have little tendency to travel far from their origin. This is due to their high moisture content which causes rapid settling (Matthews 1979).

Limited quantities of water were used at Hanna, primarily for smelting (i.e., for ore belt washing), scrubbers on ore driers, once-through cooling, and slag granulation. Although much of the water was recycled within the process, that which was not was serially treated in two settling ponds. The first pond released < 1 kkg of nickel to the

Table 3-2. U.S. Nickel Production and Environmental Releases, 1979 (kkg)[a]

Source	Input[b]	Contained[b]	Environmental Releases (kkg)					
			Air	Water[c]			Land	Total
				(T)	(S)	POTW		
Production and Recovery								
Primary								
Hanna Operations:[d]								
Mining/Milling	1,285,000[e]	12,800[f]	neg[g]	<1[h]	<1[h]		2,600[i]	2,600
Smelting		10,600[j]	neg[g]	<1[h]	<1[h]		neg[k]	1
AMAX Operations[m]								
Smelting/Refining		29,500	30[l]	132[l]	132[l]		132[l]	295
Secondary (scrap)								
Nonferrous Metal								
New Scrap: Ni-base		2,300	2[l]	10[l]	10[l]		10[l]	23
Cu-base		2,800	2[n]	565[o]	327[o]	237[o]	464[o]	1,031
Al-base		1,700	neg[p]	neg[p]			neg[p]	neg
Old Scrap: Ni-base		4,600	5[l]	21[l]	21[l]		21[l]	47
Cu-base		440	<1[n]	92[o]	53[o]	38[o]	75[o]	168
Al-base		160	neg[p]	neg[p]			neg[p]	neg

Footnotes next page

Table 3-2. (Concluded)

a) Totals may not add due to rounding.
b) Sibley, 1980.
c) T = total; S = surface; POTW = publicly owned treatment works; T = (S) + (POTW)
d) See Note 1, Appendix A for description of Hanna operations.
e) Total nickel-containing ore.
f) Ferronickel recovered.
g) Negligible, (i.e., <1 kkg); aerosols are not readily formed due to high moisture content of mineral, Matthews, 1979.
h) Based on 0.03 mg/l of wastewater from mining, milling, smelting, refining, combined; 453,600 l per day flow rate, 365 days per year operation, EPA, 1975b, see Appendix A, Note 2 for further details.
i) Based on plant estimates of 17% of total ore mined is discarded, Boldt, 1967; 1.2% nickel contained in ore, Matthews, 1979.
j) Total ferronickel shipped from production site; 2,200 kkg of ferronickel was stockpiled, Sibley, 1980.
k) Slag is granulated and metal values recovered by magnetic separation and charged to refining furnaces, Boldt, 1967
l) Approximately 1% of nickel input is lost during processing, Hoppe, 1977; assuming 0.001 kkg nickel emitted to air per kkg nickel produced, EPA 1973b, while the remaining wastes equally divided between water and land. Wastewater are sent to tailings pond.
m) See Note 3, Appendix A for description of AMAX operations.
n) Approximately 1 kg nickel emitted to air per metric ton of nickel charged in copper-base alloys, EPA, 1973b.
o) Based upon difference in amount of nickel wastes in treated and untreated discharges; nickel removed during treatment is disposed to land; see Appendix A, Note 5 for further details.
p) Wastes <1 kkg of nickel are considered negligible, see Table 3-4 for calculations; EPA, 1977.

environment via evapotranspiration and underflow to a nearby creek, while the second discharged approximately 5 kg of nickel to a nearby creek (see Note 2, Appendix A, for further details).

3.3.2 Refining of Imported Nickel-Containing Matte

All nickel metal produced from matte in the United States (approximately 29,500 kkg) is imported and refined by the AMAX Nickel Division in Braithwaite, Louisiana. A brief summary of the sources and compositions of the mattes that AMAX refines is shown in Table C-6, Appendix C. The refining of AMAX matte is a hydrometallurgical process; a simplified block diagram showing potential emission and discharge points is presented in Figure C-2, Appendix C.

More than 99% of the nickel contained in the initial feed material is recovered by the process (Hoppe 1977). Furthermore, because the tailings pond overflow is treated and reused in the plant, it appears that little nickel escapes during refining.

In 1979, 29,500 kkg of nickel were produced at AMAX. Assuming a release factor of 10 kg/kkg (1%), 300 kkg of nickel would have been lost, largely in the form of aerosols from matte crushing, blending, granulating, grinding, smelting, and sintering; wastewaters from cleaning refinery apparatus and ammonium sulfate crystallization processes; and solids settling in the tailings pond. Approximately 0.001 kkg of nickel was emitted to air per kkg nickel produced (EPA 1973b), thus 30 kkg of nickel were released to the atmosphere. Therefore, it is assumed that the remaining 265 kkg of nickel wastes were released to land and water sinks (i.e., 132 kkg each). No data are available concerning nickel concentrations in these wastes.

Two possible sources of nickel emissions merit further consideration. The first is nickel-containing aerosols. During the atmospheric leaching step, large volumes of air are passed through a solution which contains dissolved nickel. Because rising gas bubbles are known to selectively adsorb a variety of inorganic and organic substances, including metal ions (Piotrowicz et al. 1972) and upon bursting eject these collected materials into the air as aerosols, it is likely that atmospheric leaching produces nickel-containing aerosols.

The quantity of nickel emitted in the form of nickel-containing aerosols is dependent upon many factors, such as the concentration of nickel in the solution, density and composition of the solution, rate of bubble production, bubble size, adsorption rate, length of the path the bubbles travel before bursting, length of time the bubbles remain on the surface before bursting, composition of the gas passed through the solution, and height the jet droplets reach after ejection (Blanchard and Syzdek 1978, Wendt et al. 1979).

Because data related to these parameters were not available, no specific estimate on nickel emissions from this potential source was made.

A second source is the possibility (based upon the reduction operation) that nickel carbonyl ($Ni(CO)_4$) might be formed during nickel production. Nickel salts (in particular nickel (II) sulfate) or nickel powder, in the presence of carbon monoxide, react to form $Ni(CO)_4$ (Antonsen and Springer 1968). Therefore, if carbon monoxide is a component of feedstock hydrogen, nickel carbonyl may be produced. Data concerning the source of hydrogen used for nickel reduction and/or specific $Ni(CO)_4$ concentrations in waste gases from the reduction process are unavailable, however, and the presence (or absence) of $Ni(CO)_4$ is unconfirmed.

3.3.3 Secondary Nickel Production

Nearly all coproduct and byproduct nickel is recovered during copper (and platinum) refining and is in the form of nickel sulfate ($NiSO_4$). Although 1979 production figures for coproduct and byproduct nickel are regarded as confidential, figures are available for 1977 where coproduct and byproduct nickel accounted for approximately 5.6% of domestic production (Mathews 1979, Sibley 1980). However, extrapolation of these data to 1979 is only approximate because there is no fixed relationship between the quantity of copper (and other metals) processed and the quantity of coproduct nickel obtained.

A sample flow diagram outlining the environmental release from an electrolytic copper refinery that produces nickel sulfate as coproduct is shown in Figure C-3, Appendix C. In the above process, copper is separated from impurities by electrolytic dissolution. During electrolytic copper refining, soluble impurities tend to reach concentrations greater than optimum levels. Contaminant levels are controlled to insure optimum reaction conditions by withdrawing a portion of the spent electrolyte and replacing it with fresh solution; the decopperized solution is transferred to an evaporator for concentration and recovery of $NiSO_4$. The quantity of nickel escaping as aerosols is known to be small (i.e., < 1 kkg) because (1) relatively few plants practice $NiSO_4$ recovery (EPA 1975c), and (2) the most widely used evaporator systems are closed systems so that captured nickel-containing aerosols are recycled (Outokumpu Engineering Inc. 1980). Furthermore, it is assumed that the quantity of nickel discharged from centrifuges and slimes is negligible (< 1 kkg) because recycling to electrolytic cells and processing for metal recovery are common practices employed at such facilities (EPA 1975c).

A significant amount of the nickel produced in the United States in 1979 came from scrap metal. Basically, there are two types of scrap -- "new" and "old." New scrap is overflow or excess material generated directly from refining and it seldom reaches an outside market.

Old scrap refers to obsolete consumer products which are returned through scrap brokers to steel mills, foundries, smelters, and refineries (Matthews 1979).

Customarily, scrap is smelted, refined, and then used to make products similar in composition to those that entered the process. Ferrous scrap, for example, is recycled by iron and steel processing methods which generate no primary nickel product. Recycling of new nickel-bearing scrap can be compared directly with the processes used for primary metals, while recycling of old nickel-bearing scrap encompasses a variety of recovery procedures, each unique to the type of material being processed. In the United States, scrap high in nickel alloy is not normally used unless its composition is known within close limits so that it can be reused as is. Generally, it is exported instead (Matthews 1979).

In 1979, approximately 12,000 kkg of nickel were recovered from scrap processes at copper smelters and refineries, nonferrous metal foundries, and manufacturing plants; nearly all of this scrap was nickel-, copper-, or aluminum-base alloy, as shown in Table 3-3. Approximately 6800 and 5200 kkg of total nickel came from new and old nonferrous scrap, respectively. The steel industry also recycled approximately 40,000 kkg of nickel from stainless steel or nickel-bearing steel alloys.[1] In 1979, an estimated 6800 kkg of nickel were recovered in the United States from nickel-base scrap. Of this about 33% (2260 kkg) and 66% (4550 kkg) came from new and old scrap processing, respectively. AMAX, the only U.S. nickel refiner, produces and processes all domestic new nickel-base scrap (Matthews 1979). If AMAX recovers >99% of the nickel contained within the feed material (nickel-base scrap in this case), and roughly 2260 kkg of nickel were produced from this source, then approximately 20 kkg of nickel would be released to the environment during scrap refining (Table 3-3, Hoppe 1977, Sibley 1980). Data concerning the amount of nickel released to the environment from the refining of old nickel-base scrap is unavailable but, based on recovery values for new scrap (i.e., assuming a 1% loss), approximately 50 kkg of nickel are estimated to have been released from this source (Table 3-3; see Note 16, Appendix A, for further details).

In 1979, approximately 3300 kkg of nickel were generated from the refining of copper-base scrap where nearly 2840 and 440 kkg came from new and old scrap, respectively. Given plant wastewater flow rates and nickel concentrations of those wastewaters and assuming a 300-day work year, approximately 565 and 92 kkg of nickel were released by secondary copper smelters/refineries in untreated and treated wastewaters, respectively (Tables 3-3 and 3-4). Nickel wastes disposed to

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[1] Nickel, as referred to here, means nickel contained within an alloy, generally $\leq$ 50% by weight of that alloy (i.e., nickel-bearing steel alloy) (Adamec and Kihloren 1968, Sibley 1980).

Table 3-3. Nickel Recovered from Nonferrous Scrap, 1979 (kkg)[a]

Scrap Source	Quantity	Estimated Releases Air	 Water	 Land
New:				
Nickel-base	2,260	2[b]	10[b]	10[b]
Copper-base	2,840	2[c]	565[d]	464[d]
Aluminum-base	1,730	neg[e]	neg[e]	neg[e]
Total[f]	6,830	4	575	474
Old:				
Nickel-base	4,550	5[b]	21[b]	21[b]
Copper-base	440	1[c]	92[d]	75[d]
Aluminum-base	160	neg[e]	neg[e]	neg[e]
Total[f]	5,150	6	113	96
Grand Total[f]	12,000	10	688	570

[illegible]

Source: Sibley, 1980.

[a] Numbers rounded off to nearest ten metric tons.

[b] 1% of nickel input is lost during processing, Hoppe, 1977; based on 0.001 kkg nickel emitted to air per metric ton of nickel produced, EPA, 1973b, while the remaining wastes are equally divided between water and land.

[c] Based on 1kg nickel emitted to air per metric ton of nickel charged in copper-based alloys, EPA, 1973b.

[d] Based upon difference in amount of nickel wastes in treated and untrated discharges; nickel removed during treatment is disposed to land; see Appendix A, Note 5 for further details.

[e] Wastes amounting to less than 1 kkg are considered negligible; see Table 3-5 for calculations; EPA, 1977.

[f] Totals may not add due to rounding.

Table 3-4. Secondary Copper Production from New and Old Scrap: Nickel in Treated and Untreated Wastewaters, 1979 (kkg)[a]

PROCESS	ANNUAL UNIT FLOW (10^6 liters)[b,c]	NICKEL CONCENTRATION µg/l[c]		NICKEL DISCHARGE, kkg[d]		
		Treated	Untreated	Air	Water	Land[e]
Slag milling	19.4	1,600	3,000	neg	neg	neg
Ball mill influent	60.0	----	2,000			
Contact cooling	17.1	----	12			
Furnace scrubbers Acid tank	114	10	7,000		5	5
Waste electrolyte (electrolytic refining area cleaning water)	31.9	310,000	3,100,000		652	534
TOTAL[f]					657	539

Source: EPA, 1979a.

[a] Thirty-two secondary copper refiners are known: 7 facilities practice direct discharge; 5 practice indirect discharge; and 20 practice zero discharge. Of the 7 direct dischargers, 4 facilities treat wastewaters; of the indirect dischargers, 2 treat wastewaters; therefore, 6 plants treat their wastes while 6 do not. See Note 17, Appendix A for sample calculation.

[b] Assuming 300 days of operation per year.

[c] These values represent data for a single model plant.

[d] Discharges <1 kkg are considered to be negligible.

[e] Based upon difference in amount of nickel wastes in treated and untreated discharges, nickel removed during treatment is disposed to land.

[f] Approximately 86% and 14% of the total nickel wastes are assumed to come from old and new scrap, respectively (based on production figures).

land from secondary copper production totaled approximately 464 and 75 kkg from new and old scrap, respectively (Table 3-3). It is important to note that almost 99% of the nickel released from the above operations stemmed from combined waste electrolyte/electrolyte refining-area cleaning water.

An estimated 1890 kkg of nickel were recovered at 63 U.S. aluminum-base scrap smelters/refineries, with 1730 and 160 kkg coming from new and old scrap, respectively. Assuming a 300-day work year, <1 kkg of nickel would enter the environment from domestic secondary aluminum smelters/refineries (Table 3-5).

An estimated 6180 kkg of nickel were obtained from all the nickel-base nonferrous scrap in 1979. Assuming that the quantity of aerosolized nickel emitted per kkg of nickel-base scrap refined is the same as that from the refining of primary nickel alloy (i.e., 1 kg/kkg nickel charged), about 7 kkg of nickel were released to the atmosphere from nickel-base scrap refining (EPA 1973b). In addition, if the same emission factor is used for copper-base scrap (as is the case in the primary production of alloys composed chiefly of that metal), an estimated 3 kkg of nickel were released to the atmosphere from copper-base scrap refining.

3.3.4 Inadvertent Sources

Nickel can be released to the environment either from direct sources (i.e., those that are directly involved with the metal as in ore extraction, primary and secondary production, etc.) or from indirect or inadvertent sources. Some examples of inadvertent sources used in this chapter are coal, petroleum, and tobacco when combusted, various industrial processes such as those involved in cement and asbestos manufacture, food processing, textile and fur fabrication, laundries, and car washes. Furthermore, many foods, when consumed, act as inadvertent nickel sources. Despite the fact that nickel is present in only trace amounts in these sources, the ubiquity (and size in some cases) of these sources can make nickel releases significant when compared to those from direct production and use (see Table 3-1 and Figure C-1, in Appendix C).

3.3.4.1 Fossil Fuel Combustion

Nickel contained in fossil fuels is released from two types of emission sources--stationary and mobile (see Note 19, Appendix A, for further details). The fuels used for stationary sources are coal, petroleum, and natural gas, while mobile sources predominantly use petroleum-derived fuels. Only coal and petroleum contain significant amounts of nickel. The quantity of nickel released to air, land, and/or water is primarily dependent upon: (1) the nickel content in the feed material, (2) the apportionment of ash between fly ash and bottom ash (dependent upon boiler type), (3) the particulate removal efficiencies of control devices (if present), and (4) the nickel concentrations of the fly ash particles according to size distribution (Greenberg et al.

Table 3-5. Secondary Aluminum Production: Nickel in Treated and Untreated Wastewaters, 1979 (kkg)[a]

PROCESS	ANNUAL FLOW (10^6 l)[b]		NICKEL CONCENTRATION µg/l		NICKEL DISCHARGES[c]		
	Treated	Untreated	Treated	Untreated	Air	Land	Water
Demagging APC	5.7	114	170	<5	All Discharges Are Negligible		
Demagging APC	27	27	<50	<50			
Demagging APC	25	29	<200	<50			
Dross Milling		4.3		<5			
Contact Cooling Water	----	5.7	----	1000			

Source: EPA, 1979a.

[a] Sixty-three secondary aluminum refiners are known; 8 facilities practice direct discharge; 16 facilities practice indirect discharge; and 39 practice zero discharge. Of the direct dischargers, 6 facilities treat wateswaters. Of the indirect dischargers, 4 facilities treat wastewaters; therefore, 10 plants practice treatment.

[b] Assuming 300 days of operation per year.

[c] Discharges < 1 kkg are considered to be negligible.

1978, Lee and Duffield 1979). Further information on emission factors by boiler type and quantities of nickel released to the environment are derived in Appendix B. Environmental releases of nickel from fossil fuel combustion are shown in Table 3-6 and Table C-7, Appendix C. Also, Figure C-5 Appendix C, shows the geographical distribution of utility boilers.

In 1979, approximately 618 x 10^6 kkg of coal were consumed in the United States. Nearly 480 x 10^6 kkg (or 78%) were used by the electrical utilities, 60 x 10^6 kkg (or 10%) by industry (excluding coke ovens), 70 x 10^6 kkg (or 11%) by coke ovens, and 8 x 10^6 kkg (or 1%) by residential/commercial users (see Table C-8, Appendix C).

Upon combustion, the nickel contained within coal is distributed between two waste streams--the bottom ash stream and the flue gas stream, which contains suspended fly ash. Fly ash is removed from flue gas by control devices (e.g., electrostatic precipitators, cyclones, baghouses). These remove most of the large fly ash particles but are less efficient for removal of small particles. Both bottom ash and collected fly ash are sluiced with water to ash ponds (Slater and Hall 1977). The fly ash particles that are not captured enter the atmosphere and settle, are washed out of the atmosphere by precipitation, or remain suspended as aerosols.

Table 3-6 shows the estimated quantities of nickel released to the U.S. environment from the combustion of fossil fuels in 1979 (see Table C-7, Appendix C,for further details). Nearly 150 kkg, 7000 kkg, and 10,600 kkg of nickel were released to water, land, and air sinks, respectively. The majority of this nickel (77%) was released during the generation of electricity, while the remainder was released by coke plants (12%), space heating for industry (10%), and residential/commercial users (< 1 %).

In 1979, an estimated 1060 x 10^9 liters of refined petroleum products were used domestically. Most of that petroleum was used for transportation (564 x 10^9 liters), while the remainder was consumed by industry (211 x 10^9 liters), residential/commerical users (200 x 10^9 liters), and electrical utilities (83 x 10^9 liters). (For a discussion of fuel oils see Note 21, Appendix A.)

As in coal combustion, nickel emissions from fuel oil combustion are dependent upon many factors, including the grade of the fuel, type and size of the boiler, firing and loading practices, and the efficiencies of control devices (when present). Unlike coal-fired boilers, however, particulate control devices for fuel oil combustion are much less efficient. Based on engineering judgement and information in Note 22, Appendix A, it is estimated that approximately 50% of the ash (and, by inference, nickel) contained in fuel oils is captured by control equipment; the remainder is emitted to the atmosphere.

Table 3-6. Nickel Releases from Energy Production in the U.S. in 1979 (kkg)[a]

Source	Total Nickel	Environmental Releases				
(Contained)		Water	Land[b]	Air[c]		
				Total	<3μm	<3μm
Production						
Coal	8,300	6				
Petroleum	7,700					
Electricity Generation	9,920					
Coal	6,300	145	4,990	2,290	1,380	910
Petroleum	3,620		140	3,620	3,480	140
Space Heating and Other [d]						
Coal	1,930		1,740	620	190	160
Petroleum	4,100		160	4,100	3,940	160
Total		150	7,000	10,600		

a) Numbers may not add due to rounding; blank spaces mean <1 kkg of nickel released; see Appendix B and Table C-7, Appendix C for further details.

b) Total amount of nickel disposed to land is the sum of nickel contained in disposed bottom ash and that which is associated with particulates initially emitted to the atmosphere which settle out quickly (i.e., those >3μm in aerodynamic diameter).

c) The total quantities of nickel initially emitted to the atmosphere are listed under the total column; of the particulates that are initially emitted, only those that are <3μm remain airborne while those >3μm settle to land.

d) To include: residential, commercial and industrial users of coal and petroleum for space heating as well as coal used by coke plants and coal and petroleum used for transportation purposes.

In 1979, 564 x 10^9 liters of fuel oil were consumed in the United States for transportation purposes. The majority of this was in the form of gasoline for automobiles (Table C-7, Appendix C). There were no data available for 1979 on what percentage of the total transportation fuel was distillate oil and residual oil, but, assuming consumption to be similar to that in 1978, approximately 4% (or 23 x 10^9 liters) of the total residual fuel was used for transportation in 1979. If the density of residual oil is taken to be 944 grams per liter (EPA 1977a) and it contains on average 50 mg/kg nickel (Slater and Hall 1979), about 1000 kkg of nickel contained in the residual fuel burned for transportation were emitted to the atmosphere. The remaining transportation fuel (96% or 542 x 10^9 liters), which was distillate or higher grade, contained negligible ash and, by implication, little nickel. Therefore an insignificant amount of nickel was released from the burning of distillate fuels (see Note 7, Appendix A, for further details).

The total amount of fuel consumed in 1979 by industrial and residential/commercial users was approximately 212 x 10^9 liters and 200 x 10^9 liters, respectively. Although data are unavailable as to the consumption by fuel type, significant amounts of residual oil were used by industry, while residential/commercial users most often burned distillate fuels. Electrical utilities in the United States consumed approximately 83 x 10^9 liters (or nearly 78 x 10^6 kkg) of fuel oil, of which 92% was residual and 8% distillate. Based on a nickel concentration of residual oil of 50 mg/kg (Slater and Hall 1977), 3100 kkg of nickel are estimated to have been released to the environment from the combustion of residual oil by industry. Of this total, approximately 3000 kkg were emitted to the atmosphere as particulates which escaped control devices and remained airborne. Similarly, about 3600 kkg of nickel were released to the environment by electrical utilities burning residual fuel, of which 3480 kkg remained airborne and 140 kkg settled to land. (See Appendix B for futher details.)

3.3.4.2 Cement Manufacture

In 1979, approximately 71.6 x 10^6 kkg of cement were produced in the United States; Tables 3-7 and C-10, Appendix C, list the quantities of nickel releases to the environment from this source. Two methods are used to produce cement--dry and wet. In the dry method, the feed materials are fed to the kiln in a dry solid form. In the wet method, the feed materials are fed to the kiln as a slurry. In 1979, about 30 x 10^6 and 41.6 x 10^6 kkg of cement were produced via the dry and wet methods, respectively (assuming the apportionment between dry and wet methods to be similar to that of 1976).

The major source of environmental nickel releases from cement manufacturing processes is the kiln, followed by grinders and dryers. Typical air pollution control devices are multicyclones, electrostatic precipitators, and/or fabric filter units. Generally, nickel-containing particles are either emitted to the atmosphere after bypassing control devices or captured by the control devices and eventually dumped to landfills.

TABLE 3-7. Nickel Releases from U.S. Cement Plants, 1979 (kkg)[a]

Process	Environmental Releases (kkg)		
	Water	Air	Land
Dry kilns Dryers, Grinders	neg	143	1,872
	neg	56	737
Wet kilns Dryers, Grinders	neg	182	2,404
	neg	28	340
Total:	neg	409	5,353

a) See Table C-10, Appendix C for further details.

3.3.4.3 Miscellaneous Industries

A variety of other industries discharge small amounts of nickel (presumably to municipal treatment systems). The effluent from bakeries contains up to 0.43 mg/1 of nickel. Fur dressers and dyers also discharge effluents high in nickel concentration. These data, however, are reported in a single study of the sources of metals in New York City wastewaters. Table C-11, Appendix C, lists nickel concentrations found in wastewaters from various industries; without further data it is impossible to quantify these sources on a nationwide basis.

Nickel is found in various foods and in tobacco cigarettes; more detailed information on nickel concentrations in these products can be found in Section 4.5 - Monitoring Data and Section 5.2 - Human Exposure.

Finally, nickel is most likely released from the asbestos industry's mining operations; however, the magnitude of this source is unknown. Less than 1 kkg of nickel was probably released to the atmosphere in 1979 from this source, while possible significant amounts were released to land and water sinks via weathering of waste tailings (see Note 23, Appendix A, for further details and calculations).

3.4 USES OF NICKEL

Manufacture of nickel-containing alloys consumed approximately 157,000 kkg or 67% of the nickel supply in 1979; stainless steel production alone utilized 67,700 kkg (Sibley 1980). Approximately 27,500 kkg of pure nickel in anode form were used in electroplating. Chemical production consumed 1060 kkg, primarily in the form of nickel-containing chemicals in pigments, paints, catalysts, and fungicides. Nickel uses and releases to the environment are delineated in Table 3-8.

3.4.1 Primary and Secondary Ferrous and Nonferrous Metal Industries

Table 3-9 lists the quantities of nickel released to the environment from the major ferrous (excluding ferronickel production) and nonferrous smelting and refining industries (see Tables C-9 and C-20, Appendix C, and Note 4, Appendix A, for further details). Nearly twice as much nickel sludge was generated from ferrous industries (especially ferrosilicon dusts) as from the nonferrous industries; most of the latter's wastes were generated during primary lead smelting and secondary lead refining. For the most part, nickel sludges originating from these industries were sent to tailings ponds, sludge lagoons, landfills, or open dumps. An important alternative to disposal of these wastes is recycling. Although waste streams which are typically recycled are identified in Table C-9, Appendix C, the quantity of waste recycled is unknown but assumed to be 50%.

Various iron and steel industrial processes released nickel-containing wastewaters to water during 1979. More than ten times as much nickel was discharged to surface waters (1066 kkg) as to POTW waters (98 kkg). Furthermore, 53 kkg of nickel were emitted to the atmosphere from these industrial processes.

Table 3.8 Nickel Use and Estimated Wastes, 1979 (kkg)

Use	Quantity(kkg)[a]	Estimated Releases (kkg)				
		Air	Land	Water		
				Total	Surface	POTW
Alloys (total)	156,970	530	neg	neg		
Stainless Steel/Heat resistant	67,670	340[b]	neg	neg		
Other Steel Alloys	19,070	95[b]	neg	neg		
Super Alloys	15,400	15[c]	neg	neg		
Ni-Cu/Cu-Ni Alloys	9,790	10[c]	neg	neg		
Permanent magnet alloys	730	1[c]	neg	neg		
Other nickel alloys	41,070	40[c]	neg	neg		
Cast iron	3,240	30[d]	neg	neg		
Electroplating	27,500	neg	3,040[e]	200[f]	50	150
Batteries[g]	1,470	6[i]	3[j]	14[j]	1	13
Chemicals[h]	1,060	neg	4	3	<2	<2
Nickel brasses and bronzes	30	neg	neg	neg		

[a] Values rounded to nearest 10 kkg, Sibley, 1980; values represent quantities of nickel contained in product.

[b] Assume 5 kg Ni emitted/kkg Ni charged, EPA, 1973b.

[c] Assume 1 kg Ni emitted/kkg Ni charged, EPA, 1973b.

[d] Assume 10 kg Ni emitted/kkg Ni charged, EPA, 1973b.

[e] Assume 95% of Ni in wastewater is contained in sludge, Patterson, 1976; Masarik, 1980; and 270 kkg remaining in water after treatment; see Appendix A, Note 8.

[f] Assume 0.45 kkg Ni/plant, EPA 1979b.

[g] See Appendix A, Note 10.

[h] Includes ceramics, catalysts, and pigments.

[i] Assume 4 kg Ni emitted/kkg Ni processed as batteries, EPA, 1973b.

[j] Ni in sludge 2 kkg, Ni in scrap batteries 1 kkg, see Appendix A, Note 10.

Table 3.9.

Environmental Releases in Metric Tons (kkg) from Select Industrial Processes (1979)[a]

Process/Waste	Environmental Releases (kkg)			
	Land	Water		Air
		Surface	POTW	
Ferrous Metal Smelting and Refining				
Iron and steel production				52[b]
Ammonia still lime sludge	0.25			
Basic oxygen furnace emission control sludge	31			
Open hearth furnace emission control dust	29			
Electric furnace emission control sludge	24			
Rolling mill sludge	39			
	6			
Cold rolling acid rinsewater neutralization sludge	1.5			
Cold rolling mill waste H_2SO_4 pickle liquor	41			
Cold rolling mill waste HCl pickle liquor	3			
Galvanizing mill H_2SO_4 rinsewater neutralization sludge	7			
Galvanizing mill HCl rinsewater neutralization sludge	2			
Decanter tank tar	2			
Ferrosilicon manufacture dusts	1,078			
Ironmaking		7		
Sintering		5		
Hot Forming (pipe/tube carbon)		37		
Hot Forming (pipe/tube specialty)		6		
Scale Removal (kolene specialty)				
Scale Removal (hydride)				
H_2SO_4 Pickling Batch (carbon-specialty)		3		
H_2SO_4 Pickling Continuous (carbon-specialty)				
HCl Pickling Batch (carbon-specialty)				
HCl Pickling Continuous (carbon-specialty)		14	6	
Combined Pickling Batch (carbon-specialty)		2		
Combined Pickling Continuous (carbon-specialty)		14		
Cold Forming (cold roll recirculating, carbon-specialty)		2		
Cold Forming (cold roll combination, carbon-specialty)		6		
Cold Forming (cold roll direct application, carbon-specialty)		25		
Hot Coating (galvanized strip sheet and misc.)		7	3	
Hot Coating (galvanized wire, wire products)		3	2	
Hot Coating (terne, continuous strip sheet only)				
Hot Coating (other metalling coat, continuous/batch, strip sheet)		2		
Hot Coating (other metallic coating, continuous/batch wire)				
Hot Forming (primary carbon with scarfers)		119	7	
Hot Forming (primary specialty without scarfers)		24	1	
Hot Forming (primary specialty with scarfers)		9		
Hot Forming (section, specialty)		77	34	
Hot Forming (flat/strip, carbon specialty)		389	20	
Hot Forming (flat plate carbon)		52	5	
Hot Forming (section carbon)		258	20	
BOF (wet suppressed, carbon and specialty)				
BOF (wet open, carbon and specialty)		3		
Open Hearth (semiwet)				
Electric Arc (wet, carbon and specialty)				
Vacuum Degassing (carbon and specialty)				
Primary Nonferrous Smelting and Refining				
Copper smelting				
Acid plant blowdown sludge	0.4			
Reverberatory furnace				
Electrolytic copper refining				1
Mixed sludge	0.4			
Lead smelting				
Acid plant blowdown sludges	522			
Electrolytic antimony manufacture				
Spent anode sludge	14			
Secondary Nonferrous Refining				
Lead refining				
SO_2 scrubwater sludge	164			
TOTAL	1,962	1,066	98	53

[a] See Tables C-9 and C-20 and Note 4, Appendix A for detailed calculations for land, water and air releases, respectively.

[b] This emission value represents the entire iron and steel production figure, while land and water releases are found below.

Source: EPA, 1980d.

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3.4.2 Nickel-Containing Alloys

Nickel is alloyed with base metals such as iron, copper, and molybdenum to improve strength, hardenability, and corrosion and heat resistance; alloy composition is dependent upon the specific end use. Table C-13, Appendix C, lists the composition and use of common industrial nickel alloys.

Alloys are usually manufactured by fusion of metals to form either a mixture (if the metals are mutually insoluble) or a solid solution (atoms of one metal take position in the crystal lattice of another). Nickely alloys are formed by sand, centrifugal, or investment casting. Losses of nickel from alloy manufacture are largely to the atmosphere during smelting operations. Using EPA emission factors (1973b), approximately 520 kkg of Ni were emitted to the atmosphere from alloy manufacture where stainless steel production accounted for 340 kkg or 65% of this total (Table 3-8).

Since most water used in alloy production is non-contact cooling water, aqueous nickel losses are assumed to be negligible. Nickel releases to land from this process are also assumed to be negligible because scrap metal (new scrap) is recycled within the plant.

Nickel is alloyed with other metals to provide corrosion-resistant materials; loss of nickel from use of these materials is very small, but usually occurs when these materials come in contact with acidic substances or skin (i.e., kitchen workers handling silverware). Nickel-copper alloys generally exhibit corrosion rates of less than 0.005 inches/year. Table C-18, Appendix C, lists corrosion rates for several nickel-containing alloys under various conditons.

Due to the recent increase in the cost of gold, silver, and platinum, the use of nickel in dental alloys has increased. Such alloys, when in the mouth, are slowly dissolved, releasing small quantities of nickel ions. Small quantities of nickel, in the form of dusts, are released during preparation of nickel-containing dental alloys in the dental laboratory (Huget 1980).

3.4.3 Electroplating and Electroless Plating of Nickel

Electroplating, including electroforming, electroless plating, and vapor-deposited coating, utilized 27,500 kkg of nickel as the metal anode in 1979 (Matthews 1980). Electroplating is generally used in combination with chrome plating on items such as household appliances and automobile trim, and involves surface preparation, plating, and post-plating treatment (see Figure C-6, Appendix C). Chemical compositions of common plating baths are given in Table C-14, Appendix C.

The principal source of nickel losses from both electroplating and electroless plating is carryover plating solution (into the rinse system). Discharges of nickel from spills, equipment cleaning, and disposed spent electrolyte solution are much less significant. Aerosols from air sparging of plating solutions do not appear to be large (Masarik 1980); moreover, such emissions are likely to be localized within the plating process. Wastewaters from electroplating facilities are typically treated with calcium carbonate to precipitate soluble nickel salts as nickel (II) hydroxide (see Note 24, Appendix A, for other treatment practices). This treatment method generates a large volume of sludge ($\sim 3 \times 10^6$ liters/day on an industry-wide basis) containing 2-6% solids (Masarik 1980). Based on effluent discharge data for 443 electroplating facilities (see Table C-15, Appendix C), approximately 200 kkg of nickel were discharged in 1979 of which 150 kkg were sent to POTWs. The remainder was directly discharged to rivers/river basins (EPA 1979b).

Although treatment efficiencies at electroplating facilities vary with wastewater composition, an average nickel removal efficiency of 95% has been assumed (Patterson 1976, Masarik 1980). If 200 kkg of nickel discharged as effluent represent 5% of the total wasteload, approximately 3800 kkg of nickel were discharged as sludge in 1979. Although the metal values in such sludge can be reclaimed, 80% of the electroplaters dispose the sludges to public or private landfills; the remainder is reported to be reclaimed off site. Thus, roughly 3040 kkg of nickel-containing sludge were land disposed in 1979.

3.4.4 Nickel-Based Batteries

Nickel-cadmium, nickel-iron, and nickel-zinc batteries are fabricated in the United States where the nickel-cadmium system is by far the most common (especially the sintered plate, pocket plate, and sealed forms).

As noted in Table 3-8, approximately 1470 kkg of nickel were used in battery manufacture in 1979 (Antonsen 1980). Based on an emission factor of 4 kg per kkg of nickel processed, 6 kkg are estimated to have been emitted to the atmosphere from battery manufacture (sintering process) (EPA 1973b).

Waterborne nickel discharges are a result of washing and rinsing battery plates. Based on an average discharge from two plants (after treatment) of 15 kg nickel/kkg of batteries produced and a total production of 890 kkg, approximately 13 kkg of nickel were discharged to POTWS from battery manufacture (EPA 1976). The eight remaining production facilities practiced direct discharge. Based on an average discharge of 0.01 kg of nickel/kkg batteries produced, <1 kkg of nickel was discharged directly to surface waters (EPA 1976).

Wastewater sludge and scrap batteries are sources of nickel-containing solid wastes. Sludge, which contains an estimated 12% Ni (dry basis), was sent to settling ponds at 2 of 10 plants and released approximately 1.7 kg Ni/kkg batteries produced (EPA 1975a). If the 2 plants produced a total of 890 kkg of batteries, approximately 2 kkg of Ni (as $Ni(OH)_2$) were released to landfills as sludge. Scrap battery cells are usually sold to scrap reclaimers; in 1975, only 2 of 10 NiCa battery plants practiced land disposal of scrap cells (EPA 1975a). Assuming these disposal practices to be similar to those in 1979, a release factor of 1.5 kg Ni/kkg batteries produced and total production of 890 kkg, approximately 1 kkg of nickel was sent to landfills in the form of scrap batteries (EPA 1975a).

3.4.5 Nickel Chemicals and Catalysts

The majority of the commercially important nickel compounds are of the Ni(II) species; the industrially significant compounds are listed in Table C-16, Appendix C. Nickel sulfate and nickel chloride are the major constituents of electroplating baths. Nickel carbonyl is primarily used as an intermediate in high purity nickel production and as a catalyst. Nickel oxide is used to impart a grey-green color to glass and ceramics, serves as an intermediate in the manufacture of most nickel-containing chemicals, and is used in stainless steel manufacture.

3.4.5.1 Nickel Compounds

Nickel sulfate, used primarily in electroplating baths and to a small extent in fungicides, is produced from nickel or nickel oxide or is recovered from spent plating solutions. According to the most recent information available (from the Census of Manufactures), approximately 6400 kkg of nickel sulfate were manufactured domestically in 1977 (Schlotterbeck 1980). Atmospheric emissions of nickel from production of nickel sulfate were negligible because dusts from dryers and product packaging operations were collected and sent to a scrubber. Furthermore, engineering estimates of wastewater and sludge releases from nickel sulfate manufacturing plants indicate that approximately 3 kkg of nickel were released to each land and water in 1979 (EPA 1977b). Such estimates seem resonable because filtration sludges were reprocessed to recover nickel and treatment tank liquors were recycled. Environmental releases from its use in the electroplating industry have already been reported in Section 3.4.3. Nickel sulfate is also incorporated into select fungicides (manufacturers of $NiSO_4$-containing fungicides, their locations, and product compositions are listed in Table C-19, Appendix C). Environmental releases from nickel containing fungicide use are unavailable but assumed to be <1 kkg.

Nickel chloride, also used in electroplating baths, is prepared by chlorination of nickel oxide with Cl_2 (Antonsen and Springer 1968). Though production data are unavailable for 1979, a J. T. Baker Chemical Company representative estimated their annual company production to be <20 kkg (Bishop 1980), while an Allied Chemical Corporation representative estimated annual production to be <5 kkg (Swan 1980).

Nickel-containing pigments include nickel azo yellow, nickel antimony titanate, and nickel dimethylglyoxime (see Note 25, Appendix A, for discussion of pigments). Although production figures for azo yellow were unavailable, a Ciba Geigy spokesperson estimated their production to be 4 kkg in aqueous form and 0.5 kkg as a dry powder (Malaga 1980).

Nickel antimony titanate is a large-volume yellow latex paint pigment. A spokesperson from Harshaw Chemical Company estimated nationwide consumption of this pigment to be 1350 kkg, approximately 50% of which is imported (Dickinson 1980).

No specific data concerning manufacture and use of nickel-containing dyes or pigments were found. The nickel concentration of wastewater treatment sludge from woven fabric dying and finishing facilities ranges from 12 to 88 mg/l. Assuming a total sludge production of 28,000 kkg/yr and sludge composition of 95% water, a maximum of 2 kkg of nickel would be released to the environment from sludge disposal (Viviani 1980).

Nickel carbonyl can be prepared by reacting carbon monoxide (CO) with nickel powder or by reacting CO with nickel salts in solutions. Nickel carbonyl has been used as a reactant in the production of acrylic and acid from acetylene; however in recent years, this process has been superceded by direct oxidation of propene (Antonsen 1980). Decomposition of $Ni(CO)_4$ produces high purity nickel used in powder metallurgy, and represents the most significant industrial application of the compound.

Nickel oxide is prepared by heating the metal in oxygen at temperatures above 400°C. Although nickel oxide is not produced domestically, approximately 6800 kkg reached the U.S. market in 1979 from a Canadian producer (Antonsen 1980). Because nickel oxide is converted (or contained) during use (i.e., an intermediate in chemical synthesis or bound in ceramic, glass, enamel, and steel products), it is unlikely that >1 kkg of nickel was released to the environment.

3.4.5.2 Nickel Catalysts

Commercial applications of nickel catalysts include hydrotreating, coal gasification, and hydrogenation of various fats and oils (see Note 26, Appendix A, for further details). Production data on nickel hydrotreating catalysts are unavailable, however, roughly 6800 kkg of this class of catalysts were consumed in 1979. Of this, 25% was estimated to be nickel based. Assuming 10% of the catalyst weight to be nickel, 170 kkg of nickel were used in hydrotreating catalysts. Losses during hydrotreatment of crude oils are estimated to be on the order of 10 kg/kkg or 2 kkg for 1979.

During indirect liquefaction, coal is gasified to a mixture of $CO+H_2$ and catalytically converted to fuel products. Using a reduced nickel catalyst and proper operating parameters, methane is the only product (Mills and Cusumano 1979). For a plant producing 2.5 x 10^{10} kkg fuel/day, approximately 10 kkg of spent catalyst would be discharged annually (EPA 1980a).

Hydrogenation of oils or partially solid fats to produce margarines, shortenings, and confectionary fats is an important application of nickel catalysts. For most edible applications, 0.02-0.15 grams of nickel are used per 100 grams of oil charged. In batch hydrogenation, the catalyst can be reused a number of times, often in combination with small amounts of fresh catalyst. Spent catalyst is regenerated by oxidation and subsequent reduction. The most recent data concerning catalyst usage are provided by Burke (1972) who reports that approximately 2300 to 2700 kkg and 700 kkg of 25% nickel catalyst (or 575 to 625 kkg and 175 kkg of nickel, respectively) were used in hydrogenation of edible and inedible oils, respectively.

3.5 DISPOSAL OF NICKEL-CONTAINING WASTES

This section deals with the ultimate disposition of nickel released to municipal waste facilities: publicaly owned treatment works, urban refuse landfills, and incinerators. A summary materials balance around each waste treatment category is shown in Table 3-10.

3.5.1 Publicly Owned Treatment Works (POTWs)

Nickel loading to POTWs is largely dependent upon variations in industrial discharges and the types of industry in a municipal area. Based on calculations shown in Note 27, Appendix A, approximately 960-2600 kkg of nickel were disposed to land (as sludge) from POTWs in 1979, 3900 kkg of nickel were released to water environments from the same source, and < 1 kkg was emitted to the atmosphere (Table 3-10).

3.5.2 Urban Refuse

Urban refuse, divided into combustible and non-combustible fractions, is usually landfilled (87%), recycled (8%), or incincerated (5%) (Geswein 1980, Alvarex 1980). A flow diagram for nickel through a municipal incinerator with a capacity of 920 kkg dry refuse per week is illustrated in Figure C-7, Appendix C. Assuming 10^7 kkg of solid waste were incinerated in 1979, an estimated 110, 540, and 2 kkg of nickel were released to air, land, and water, respectively (Law and Gordon 1979, EPA 1976).

Landfill losses of nickel are more difficult to quantify due to the exceedingly large number of sources and variety of materials. Of the 1.0 x 10^7 kkg of municipal solid waste produced in 1979, approximately 10% (by weight) is metal, with 1% being nonferrous metal (Gordon 1978). No information is available as to what percent of this nonferrous group is nickel. Also, studies concerning concentrations of nickel in either municipal or industrial landfill leachates could not be found (see Note 28, Appendix A, for further details).

Table 3-10. Municipal Disposal of Nickel, 1979 (kkg)

Source	Input	Environmental Releases		
		Air	Water	Land
POTW[a]	6570	neg[b]	3900[c]	2660[d]
URBAN REFUSE				900[e]
INCINERATION	650	110[f]	2[g]	540[h]
LANDFILL				

a) Publicly-owned treatment works.
b) Atmospheric loss assumed to be less than 1 kkg.
c) Assume average effluent concentration to be 0.107 µg/l and 10^{11} l/day to be the total POTW flow rate, EPA, 1978c.
d) Based on 5.5 x 10^6 kkg dry sludge produced/yr, sludge is 95% water by weight, and 8 mg of nickel/l in wet sludge; EPA, 1979d.
e) Assume Ni in sludge is difference of influent and effluent concentrations (Table C-17) with total flow of 10^{11} l/day; EPA 1980b.
f) Assume 1 kg Ni emitted/920 kkg, 10^7 kkg incinerated, Law and Gordon, 1979; EPA, 1976.
g) Assume 0.2 kg Ni discharged/920 kkg, 10^7 kkg incinerated, Law and Gordon, 1979; EPA, 1976.
h) Assume 50 kg Ni discharged/920 kkg, 10^7 kkg incinerated, Law and Gordon, 1979; EPA, 1976.

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4.0 ENVIRONMENTAL PATHWAYS

4.1 INTRODUCTION

This chapter discusses the fate of nickel in the environment, its biological fate, and monitoring data.

4.2 CHEMICAL PROPERTIES

Nickel is a silvery white, ductile, corrosion-resistant metal, usually found associated with sulfide, silicate, or arsenide minerals in nature. It combines with most common metals to form alloys; Monel, for example, is an alloy of nickel and copper used for handling flourine and corrosive flourides.

A descriptive review of the chemistry of nickel is given by Nicholls (1973). This section will deal with properties that could have some environmental significance. The five isotopes of nickel commonly found in nature are ^{58}Ni, ^{60}Ni, ^{61}Ni, ^{62}Ni, and ^{64}Ni. None of the common isotopes are radioactive. ^{58}Ni makes up an estimated 68% of the known isotopes, while ^{58}Ni and ^{60}Ni together form approximately 95% of the known isotopes. The most common oxidative state of nickel is +2 although other states (-1, 0, +1, +2, +3, and +4) are known. Nickel is dissolved slowly by dilute, non-oxidizing acids, liberating hydrogen. Dilute nitric acid dissolves nickel rapidly with the evolution of nitrogen oxides. Concentrated nitric acid, however, does not attack nickel readily due to the formation of an oxide film on the metal. Nickel is very resistant to caustic alkalis but not to aqueous ammonia.

Nickel carbonyl, $Ni(CO)_4$, may be found wherever carbon monoxide contacts nickel and nickel alloys (IARC 1976) and as a product of fossil fuel combustion (IARC 1973). Pure nickel carbonyl is a mobile, colorless, highly volatile liquid under ordinary conditions (Hygienic Guide Series 1968). In dry air, it decomposes readily to form nickel oxide, but under moist conditions, nickel carbonate is found (IARC 1973). Both these decomposition products are insoluble in water. The carbon monoxide in nickel carbonyl may be replaced by other molecules such as phosphines, arsines, stribines, isonitriles, and nitric oxide (Standen 1967). Nickel carbonate occurs in nature as the mineral zaratite, $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ (IARC 1973). Nickel subsulfide is found in nature as the mineral heazlewoodite (IARC 1973); it is not soluble in water. Nickel sulfate however is very soluble in water (IARC 1976).

Organic compounds possessing acidic or basic functional groups, such as COOH, phenolic OH, SH, SO_3H, POH, trivalent nitrogen, phosphorus, arsenic, oxygen (in ethers), and sulfate (in thioethers), may react with nickel to form derivates of these organics (Standen, 1967).

This property of nickel is important in anaerobic environments which result in acidic conditions.

4.3 ENVIRONMENTAL FATE

This section covers the fate of nickel in the various environmental media. The behavior of nickel in soils is discussed in the context of mining activities, agricultural application of POTW sludge, landfills, wet and dry deposition. Waterborne nickel occurs as a result of POTW discharges, industrial wastewater discharges, and natural sediment loads to streams. Nickel is released to the air by industrial activities, municipal waste and sludge incineration, and natural erosion of ground materials.

4.3.1 Entrainment, Runoff, and Leaching

4.3.1.1 Tailings and Mining Wastes

During mining operations nickel is lost to the environment through area runoff and disposal of residual rocks and submarginal ore. Nickel ores do not have a tendency to dust because of high moisture content. The quantities of nickel discharged through wastewater and as solid waste are unknown, but solid waste for mining operations is expected to be significant (Versar, Inc. 1977).

4.3.1.2 Application of POTW Sludge to Farmland

Heavy metal concentrations in POTW sludges and in soil and crops from sites where sludges were applied to farmland have been reported by Chaney et al. (1977) for 43 treatment plants in the northeastern United States. The mean concentration of nickel in sludges from all 43 plants was 129 mg/kg (mg/kg dry sludge), with a median value of 42 mg/kg. These values were lower than those for the other heavy metals studied, except cadmium (mean = 72.2 mg/kg). Where sludges high in nickel were used, levels of nickel in crops and plant leaves were higher only at low soil pH. Soybean seeds, in particular, were observed to accumulate nickel from the sludge-amended soils.

4.3.1.3 Landfills

Reported landfill leachate compositions vary widely. Boyle and Ham (1974) cite a number of reasons for this, including refuse characteristics, hydrogeology of the site, climate, slope, age of the site, height of the refuse, and moisture seeping through the refuse. They note, in addition, that the quantity of leachate from a sanitary landfill site is also highly variable, depending on the design of the landfill and the method of operation and management. In any case, straight municipal solid waste leachate is characteristically low in heavy metals (Alesh et al. 1980). Nickel concentrations in typical "municipal solid waste leachate" are reported as 0.01 - 0.8 mg/l (Steiner et al. 1971); the highest reported concentration is 13 mg/l (Chian and DeWalle 1977). Higher concentrations may be observed in leachates from landfills where co-disposal of municipal and hazardous waste occurs.

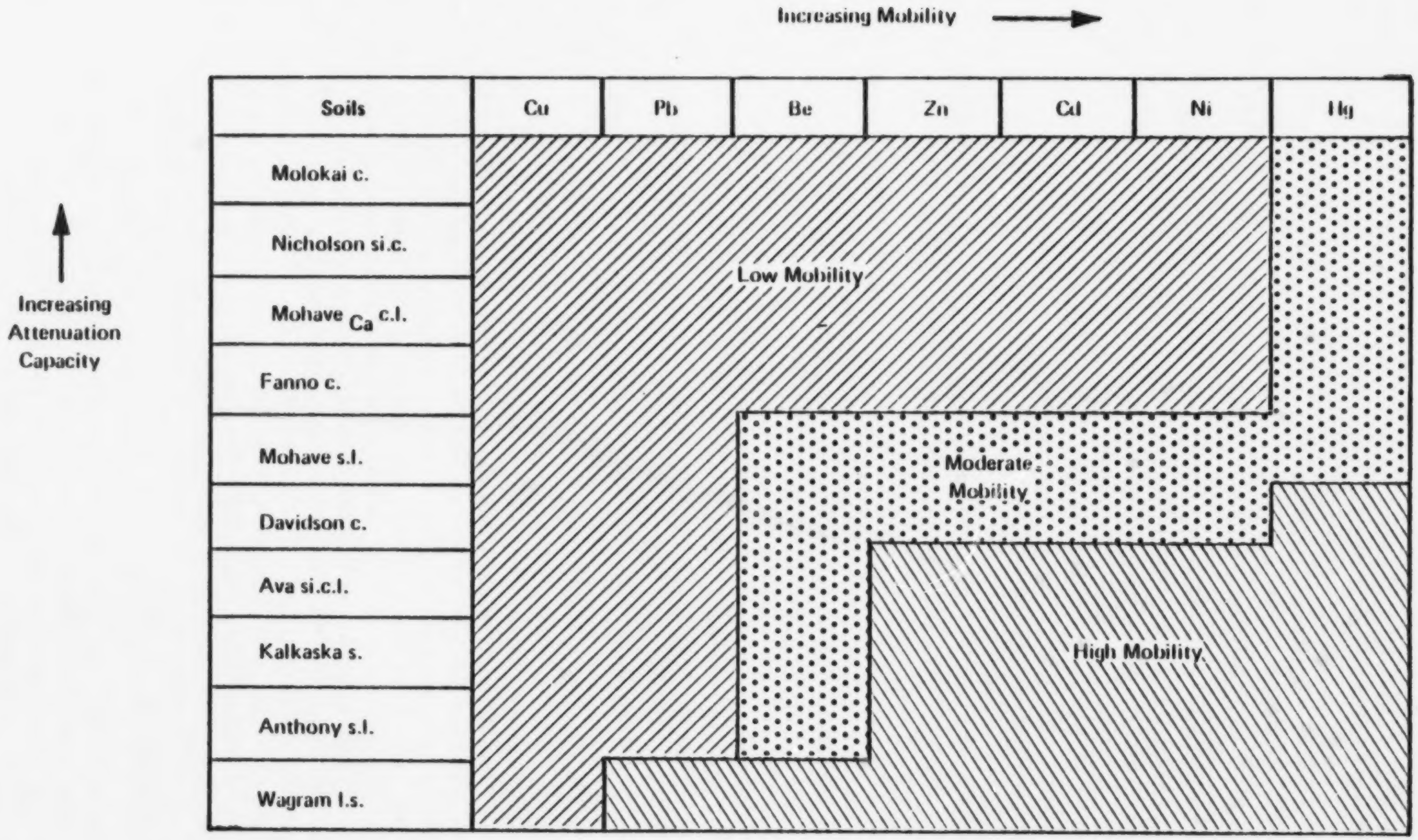
Fuller (1977) evaluated the relative mobility of a number of heavy metals in soil-column leaching experiments using natural municipal solid waste leachates and 10 soils representative of 7 major soil orders in the United States. Nickel, chromium, and mercury were classified as the most generally mobile of the 11 metals studied (only 7 are shown in Figure 4-1). Soil clay content was one of the soil properties most useful in predicting the attenuation of contaminants by soils. Figure 4-1 is a qualitative summary of the results of the study. In the figure soils used in the study are ranked according to their attenuation properties, and metals are ranked according to their mobility in the various soils.

In another series of soil-column leaching experiments intended to study the effect of leachate flow rate on metal migration from soil, leachate flow rate was found to have little effect on the attenuation of nickel, cadmium, and zinc in 7 subsoils which represented 7 of the 10 major orders in the United States (Alesh et al. 1980). For the same three elements, mobility, expressed as the number of pore volumes necessary to achieve breakthrough, was found to be similar for similar soils. Relatively lower mobilities were observed for each element in soils with higher clay content, which is consistent with Fuller's findings.

In a separate series of column leaching experiments in which only cadmium was measured, the migration rate was found to be independent of the leachate flow rate in influent cadmium concentration, however, the concentration of cadmium in the solution determined the amount retained by the soil (Alesh et al., 1980). These investigators concluded that the amount of cadmium, nickel, and zinc in leachate influences more than any other single factor, except perhaps the clay content, the absolute amount of the element retained. These findings suggest that nickel in landfill leachate may be relatively more mobile in the soil than certain other heavy metals. The principal soil characteristic affecting nickel migration is clay content; the amount of nickel retained by a given soil type is apparently dependent on clay content and on the concentration of nickel in the influent leachate.

4.3.2 Wet and Dry Deposition

Elevated levels of nickel in the atmosphere attributable to smelting and refining operations have been detected up to 50 kilometers away from a Canadian smelter, and in surface waters up to 15 kilometers away (Versar, Inc. 1977). Surface soil contamination patterns shown in chemical analyses of rainfall and dustfall indicate that airborne emissions are the major source of nickel to soil.



Source: Fuller (1977).

c. = clay
si.c. = silty clay
c.l. = clay loam
s.l. = silt loam
s. = sand
l.s. = loamy sand

FIGURE 4–1 RELATIVE MOBILITY OF CATIONS IN SOILS

A study of the distribution of various contaminants, including nickel, in surface soils near a nickel smelter in Coniston, Ontario, showed that the extent of nickel contamination was dependent upon distance from the smelter, exposure of the site with respect to the smelter, and soil drainage status.

Soil contamination, expressed as total metal content, decreased with distance from the smelter in a manner consistent with contaminant dispersal from the point source. Major contamination was restricted primarily to surface soils and heavy metal content generally decreased with soil depth. Secondary maxima in some profiles were attributed to leaching of metal ions, accumulation of organic matter, or the erosional/depositional history of the site. In general, most soils in the area had been physically eroded so that the original subsurface horizons were at the surface. Thus on erosional sites, periodic or continual removal of surface materials resulted in contaminated surface layers overlying weakly contaminated or uncontaminated horizons. On depositional sites, the degree of contamination through the profile would be expected to be more uniform. This was clearly demonstrated by the marked decrease in total nickel for depth in the erosional profile of at least one soil area in the vicinity of the smelter, as compared to the modest decrease in the deposition profile in another area.

A relationship between contaminant dispersal and wind transport over complex relief in the area of the Coniston smelter was apparent. The importance of exposure decreased with increasing distance from the smelter (Rutherford and Bray 1979).

Poorly drained soils showed elevated amounts of available nickel. The authors attributed this to the anaerobic conditions prevailing in such environments which result in increased production of organic acids. These acids complex with nickel and leave it in an available form. No relationship was found between the clay content of soils and available nickel.

Another study of soil contamination in the vicinity of the Coniston smelter compared that area to areas near other copper-nickel smelters in Sudbury, Ontario. The study confirmed the presence of elevated levels of nickel at distances in excess of 50 kilometers in any direction from the smelter stacks. The highest levels were found closest to the stacks. Chemical analysis of rainfall collected at various distances from the smelter indicated that airborne deposition of nickel was an ongoing process. Nickel concentrations in filtered rainwater decreased from about 300 mg/m^2, 1.7 kilometers south of the Coniston smelter to about 10 mg/m^2, 20.4 kilometers east, and 2 mg/m^2, 13.4 kilometers south.

The rainwater data are on a combination of overall dry deposition and wet deposition over the sampling period. Since rainfall was likely to have been similar over the area sampled, the results reflected a dilution effect. In the months of highest rainfall, overall metal precipitation was higher closest to the smelter stacks, suggesting that wet deposition was effective in removing metals. However, since in terms of time rainfall is a relatively rare event, dry deposition was likely to have been a predominant factor influencing nickel deposition in soil.

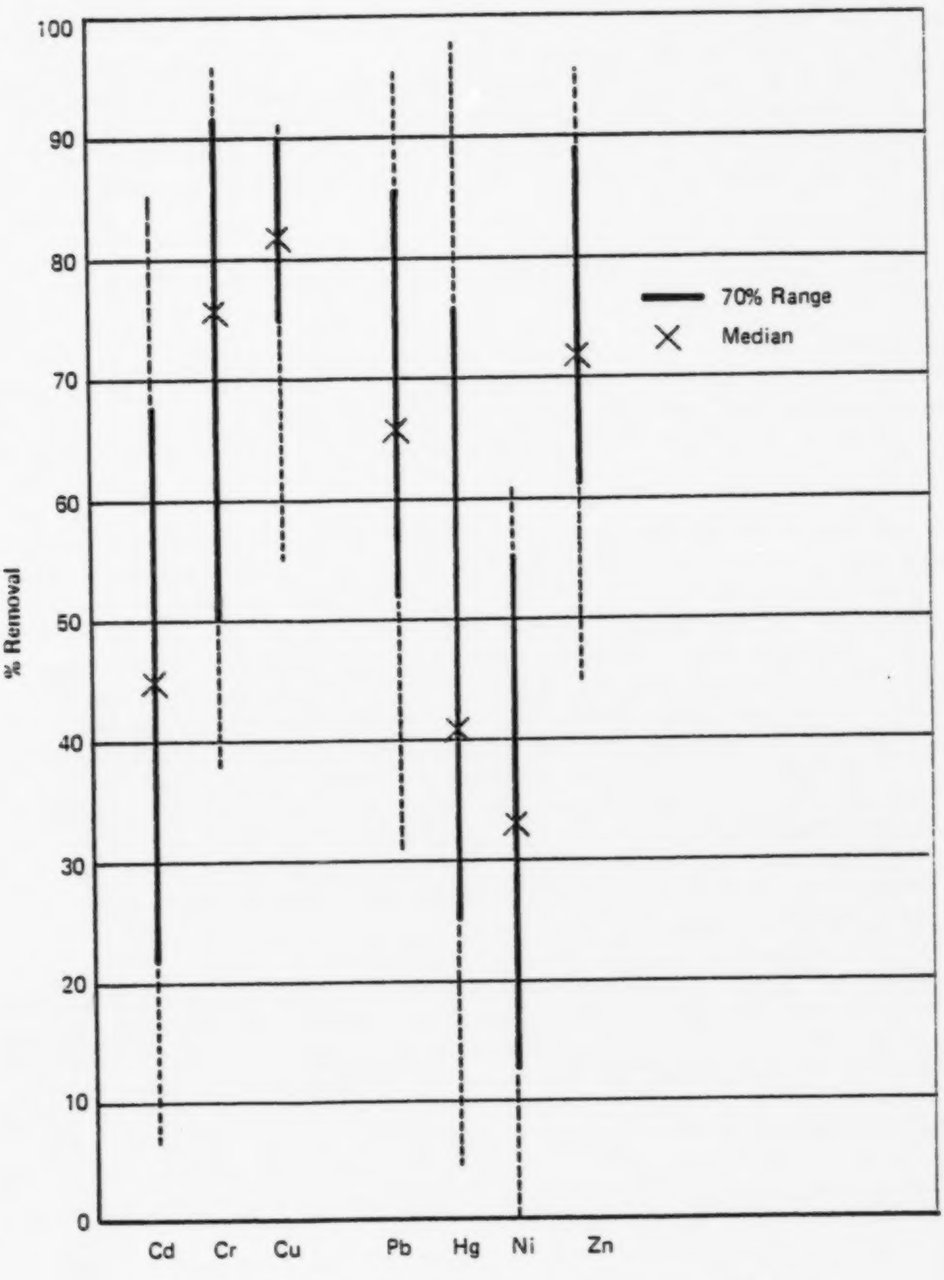
Similar patterns of soil contamination by nickel were found in the vicinity of a lead smelting complex in Kellogg, Idaho (Ragaini et al. 1977). The mean surface soil nickel concentration at seven sampling sites was 1200 µg/g; nickel concentration decreased sharply with depth. Thus mean concentration is on the same order as that observed at corresponding distances from the Coniston nickel smelter.

4.3.3 POTWs

The median nickel concentration in POTW influent in a number of sewage treatment plants surveyed by the U.S. EPA is approximately 85 µg/l, which is slightly less but on the same order of magnitude as the heavy metals, chromium (100 µg/l), copper (120 µg/l), lead (55 µg/l), and zinc (300 µg/l), and greater than the influent concentration of cadmium (12 µg/l) (U.S. EPA 1978). This reported nickel concentration is consistent with values reported by other investigators in the United States (Mytelka et al. 1973) and abroad (Stoveland et al. 1979), and is less than the threshold concentrations of 1.0 mg/l to 2.5 mg/l reported by the EPA to be inhibitory to biological treatment processes (U.S. EPA 1978).

As part of the study noted above, EPA (1978) surveyed the effluents of 22 POTWs (a mix of primary and activated sludge POTWs) and found that the median POTW nickel removal efficiency was 33%, with a range of 0% to 60%. These findings were consistent with those reported by Mytelka (1973) and Stoveland (1979); however, this median value was lower than those for all other heavy metals reported in the EPA survey (see Figure 4-2). Higher removal efficiencies at lower influent nickel concentrations have been demonstrated (U.S. EPA 1978).

Removal efficiencies vary considerably both among POTWs and within a given POTW and the factors which cause these variations are not well understood. Removal at the primary sedimentation state is considered to be dependent upon whether the nickel is present in an insoluble form or in a form which permits it to bind to the settlable solids (Stoveland et al. 1979). The presence of nickel predominantly in a soluble form was cited as the explanation for its lower removal at one POTW in the EPA survey. Attempts to correlate metal removed with other factors, such as pH, mixed liquor, suspended solids, and BOD removal, were unsuccessful. Average percentage of removal in the primary sedimentation stage at one POTW was reported to be 23% (Stoveland et al. 1979). At the same POTW, 61% of the influent nickel concentration



Source: U.S. EPA (1978).

FIGURE 4-2 POTW REMOVAL EFFICIENCIES FOR HEAVY METALS

was removed in the activated sludge process. The net average removal efficiency of 70% was comparable to that for chromium and zinc, but for those two metals a larger (chromium) or equal (zinc) percentage was removed in the primary sedimentation stage. The investigators conclude that the high removal efficiency for nickel is indicative of high concentrations of insoluble nickel as opposed to soluble nickel, and that the observed variation and removal efficiency at both stages of treatment suggest that this equilibrium is easily influenced.

4.3.4 Contribution of Nickel-Containing Wastewater Discharges to Water and Sediments

The nickel content of sea water ranges from 0.1 μg/l to 0.5 μg/l (NAS 1975). Nickel has not been identified in the majority of groundwater supplies surveyed and, in the instances where it has been detected, analysts theorize that it probably exists in colloidal rather than dissolved form (USGS 1970).

In the rock-weathering process, it has been determined that nickel goes into the insoluble minerals of the hydrolysates. Thus Kopp and Kroner (1967) concluded that any nickel in surface or groundwaters is likely to be in small amounts unless its presence is due to industrial pollution. These investigators report that the mean concentrations of nickel in major river basins in the United States range from 3 μg/l to about 60 μg/l (see Table 4-1). These values are of the same order of magnitude as those reported in the STORET Water Quality System (see Section 4.5 - Monitoring Data). Samples in which nickel was not detected accounted for the largest percentage of samples from each river basin. These samples were not used in calculating mean concentrations, so that reported nickel concentrations may accurately reflect industrial wastewater and airborne particulate discharges within the respective basins.

A number of other studies show increased nickel concentrations in surface waters and sediments which are attributed to sources associated with man's activities. Maxima in nickel concentration versus sediment depth profiles in two lakes in the vicinity of New Haven, Connecticut have been correlated through sediment deposition records with airborne nickel input emanating from fossil-fuel burning power plants in the area (Bertine and Mendeck 1978). These concentration maxima represent nickel concentrations of 60 μg/g to 100 μg/g (weight of nickel per dry weight sample) in the sediments. Acid-extractable nickel content of polluted surface horizons of sediment cores from Ticonderoga Bay of Lake Champlain were on the order of 3 μg/g to 5 μg/g as compared to concentrations generally on the order of 1 μg/g or less in corresponding samples from unpolluted lakes in the Adirondack region of New York State (Williams et al. 1977). These areas are currently being studied further to determine the effect of acid on the metal concentrations of the lakes.

TABLE 4-1. NICKEL IN WATER FROM MAJOR RIVER BASINS OF THE UNITED STATES[a]

River Basin	Mean Nickel Concentration (μg/1)[b]	Frequency of Detection (%)
Northeast	8	22.0
North Atlantic	8	28.1
Southeast	4	20.9
Tennessee River	4	8.8
Ohio River	31	25.2
Lake Erie	56	53.2
Upper Mississippi	15	15.2
Western Great Lakes	10	9.1
Missouri River	5	2.0
Southwest-Lower Mississippi	17	9.7
Colorado River	12	8.0
Western Gulf	3	2.1
Pacific Northwest	10	10.5
California	10	13.8
Great Basin	4	15.8
Alaska	5	11.1

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[a] Derived from Kopp and Kroner (1967).

[b] Only occurrences of nickel were used in calculating the mean.

Source: NAS (1975)

A statistically significant increase in the concentration of nickel in surface sediments (14 µg/g dry weight as compared to 9.3 µg/g dry weight in control samples) was observed in samples collected from the vicinity of an effluent discharge point within one month of the commencement of continuous discharge of liquid wastes from tailings settling ponds of the Queensland Nickel Pty. Ltd. nickel refinery in North Queensland, Australia. Nickel was also found in sediments of a stream ecosystem in the vicinity of a U.S. highway with average traffic density of 15,000 vehicles per day in concentrations on the order of 2 µg/g. Sediment loads of nickel, lead, and zinc were all highly correlated to the traffic volumes received by the study area. The authors attribute the nickel to highway runoff containing diesel fuel and lubricating oil (van Hessel et al. 1979). In contrast, the concentrations of nickel in sediments in the vicinity of sewage treatment plant outfalls in Puget Sound, Washington (Schell and Nevissi 1977) and in Southern California (Galloway 1979) showed little or no enrichment relative to control areas. The authors of the latter study attribute the absence of nickel enrichment in sediments to the fact that in the highly reducing effluent medium nickel is present principally as the soluble sulfide.

In each of the studies described above where enrichment of nickel in the surface horizon of sediment core samples was observed, the concentration of nickel in overlying waters was lower by factors of 2 (Williams et al. 1977) to 200 (van Hessel et al. 1979). The variation is due to the study location and level of industrial or urban activity in the surrounding area. Suspended solid samples were also relatively higher in nickel concentrations than were corresponding water samples (van Hessel et al. 1979, Leland 1975). These observations suggest that adsorption of nickel on mineral surfaces is an important control on nickel concentration. However, the amount of nickel remaining in solution is substantially greater. Galloway (1979) has calculated that the input of nickel into the oceans from the industrial world's municipal wastewater is 17×10^3 kkg/yr, which is greater than the nickel input due to natural weathering (11×10^3 kkg/yr). The natural rate of injection in the environment is constant, while the artificial injection of nickel by way of wastewater effluents will increase with the time which, as Galloway points out, may lead to substantial alteration in the geochemical cycle of nickel with possible effects on marine life.

4.3.5 Nickel in Air

Nickel enters the atmosphere from a wide variety of sources. Since about 30% of all identified environmental emissions of nickel are airborne, atmospheric distributional processes are important transport mechanisms in the non-aquatic environment. Most of airborne nickel is in the form of particulate emissions from burning oil or coal or incineration of nickel-containing materials. Although little nickel is emitted by the metallurgical industry itself, there is a large and growing amount of emissions from the combustion of oil and coal. As the use of coal for electric power production rises (from about 446 million kkg in 1976 to about 840 million kkg by 1985), along with the steady demand for the home heating oils in which nickel is found, the airborne concentration of nickel will continue to grow. Table 4-2 shows the typical amount of nickel emissions in the atmosphere resulting from various manufacturing processes.

The particulate emissions of nickel span a wide range of sizes, from submicron particles to several microns in diameter. Although precise values are not available for transport ranges and mean residence time, nickel probably can be considered to have ranges and lifetimes similar to other heavy metals. The smaller particles (<3 μm) may remain suspended in the atmosphere for 7-30 days, long enough to transport them over large distances (Davidson et al. 1974).

Davidson et al. (1974) discovered in their study of trace element size-distribution in particles emitted from a coal-fired power plant that the nickel-containing particles had a median diameter of about one micron. They also observed that nickel tended to be concentrated onto the smaller sized particles, although the exact mechanism for this concentration was not determined in the study. The condensation of nickel and its compounds onto the surface of particulates is a direct function of the particle residence time. The higher concentration of nickel on the smaller particles can, therefore, be attributed to their large residence times. Gladney et al. (1976) and Coles et al. (1979) found a similar trend in their study of emissions from large coal-fired power plants. This trend is critical because of the ability of smaller particles to remain in the atmosphere longer and their eventual deep lung deposition.

Table 4-3 shows total nickel emissions from various power plants. The total amount of particulate emissions (fly ash) is further divided into particulates of mean aerodynamic diameter of less than 3 microns and greater than 3 microns. The particulates of diameter less than 3 microns are respirable and thus constitute the greatest potential hazard for human inhalation. Larger particulates have higher settling velocities and therefore are subject to wet and dry deposition.

The ground level deposition of a particulate emission is a function of the particulate diameter, the height of release, and the turbidity in the atmosphere. Several theories exist to compute the deposition and ambient concentration of airborne particulates (Slade 1968). Once the particle size distribution is known, one can estimate the deposition rate and the ambient concentration as a function of distance from the source.

A sample calculation was performed to estimate the respirable nickel concentration in the atmosphere from a hypothetical power plant using subbituminous coal. Data for the total amount of fly ash generated and the amount of nickel emitted were obtained from the coal-fired power plant trace element study by Radian Corporation (1975). The particulate sizes emitted by an electrostatic precipitator were estimated from Jacko et al. (1976). Details of the calculation and the assumptions implicit in it are given in Appendix D.

TABLE 4-2. INVENTORY OF NICKEL EMISSIONS IN THE ATMOSPHERE BY MANUFACTURING PROCESS

Manufacturing Process	Emissions in Air
Alloy Steel	5 kg/kkg of Ni processed
Battery industry	4 kg/kkg of Ni processed
Cement - dry process	0.2 kg/10^3 kkg of cement
- wet process	0.3 - 1.1 kg/10^3 kkg of cement
Coal boilers (all types)	0.3 kg/10^3 kkg of coal
Fuel oil (all types)	0.006 - 0.03 kg/10^3 kkg of oil
Municipal incineration	0.002 kg/kkg of solid waste
Nickel and copper alloys	1 kg/kkg of Ni processed
Sewage sludge incineration	0.0002-0.002 kg/kkg of solid waste
Stainless steel production	0.3 kg/kkg of stainless steel

Source: Anderson (1973).

TABLE 4-3. NICKEL DISTRIBUTION IN AIRBORNE PARTICULATES FROM ENERGY-PRODUCING FACILITIES

Fuel	Boiler Type	Nickel Distribution (% of fly ash generated)		
		Total Airborne Particulates	Particulates <3 μm	Particulates >3 μm
Coal	Pulverized	27	16	11
	Cyclone	64	48	16
	Stoker	16	5	11
Oil	All	100	92	8
Gas	All	100	90	10

Source: Davidson _et al_. (1974)

Figure 4-3 shows the total of airborne nickel and respirable nickel concentrations as functions of downwind distance. The respirable concentration has a maximum value of about 6 x 10^{-2} µg/m^3 at a distance of about 3 km from the plant. Beyond this point, the airborne concentration steadily decreases. Figure 4-4 shows the annual ground level deposition rate as a function of downwind distance. The deposition rate steadily increases and reaches a maximum at about 3 km from the plant. Beyond 10 km from the plant, the ground level deposition is very small.

In the vicinity of copper-nickel smelters and other light metallurgical industries, the ground level deposition of nickel can be much higher than indicated in Figure 4-4. This is primarily because of larger particle size and lower emission heights. Hutchinson and Whitby (1973) measured a nickel content of 271 µg/l in 28 days of rainwater. Such high rates of wet deposition are indicative of large particles and higher settling velocities. In Huntington, West Virginia, a nickel concentration of 1.2 µg/m^3 was measured near the Alloy Products Division of the International Nickel Company, Inc. This ambient air concentration was appreciably higher than the measured concentration of 0.04 µg/m^3 at six other sampling stations (Sullivan 1969).

On a national scale, burning of 500 million kkg of coal annually can result in an average ambient respirable nickel concentration in excess of 0.02 µg/m^3. Since most of the smaller particulates may remain suspended in the atmosphere for prolonged periods of time, the average concentration will continue to increase.

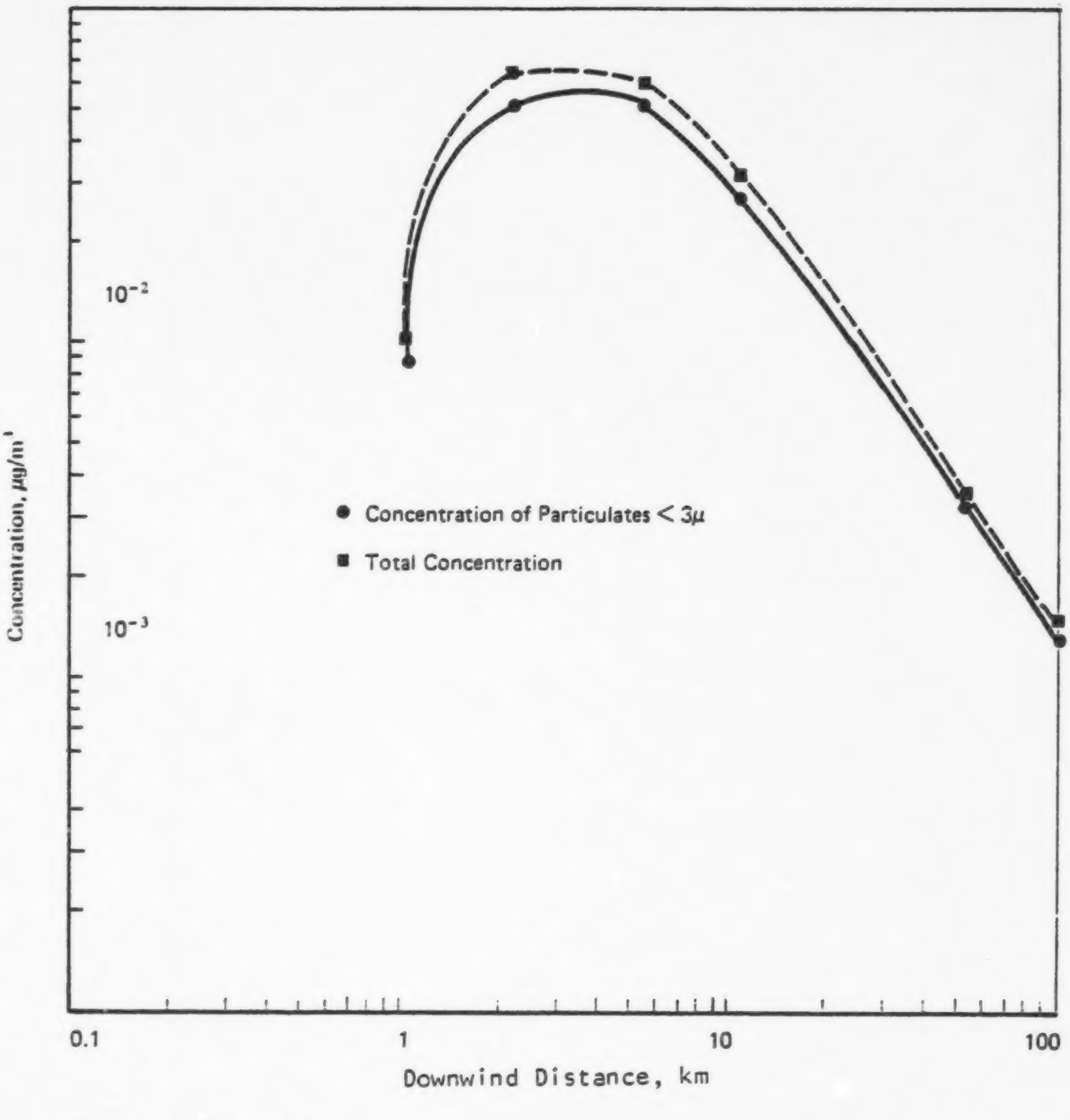
4.3.6 Summary

Air appears to be the most important transporting medium for nickel; it is estimated that over 30% of all environmental releases are atmospheric. The largest contributors of nickel to air are petroleum- and coal-burning power plants and incineration of nickel-bearing materials. Nickel is generally mobile in soils. The metal is found in low concentrations in most municipal wastes. Nickel in groundwater and surface waters has been found to be low except in areas with nearby direct industrial discharges. POTWs have variable nickel removal efficiencies, ranging from 0% to 60%, depending on the nickel load in the influent streams.

4.4 BIOLOGICAL FATE

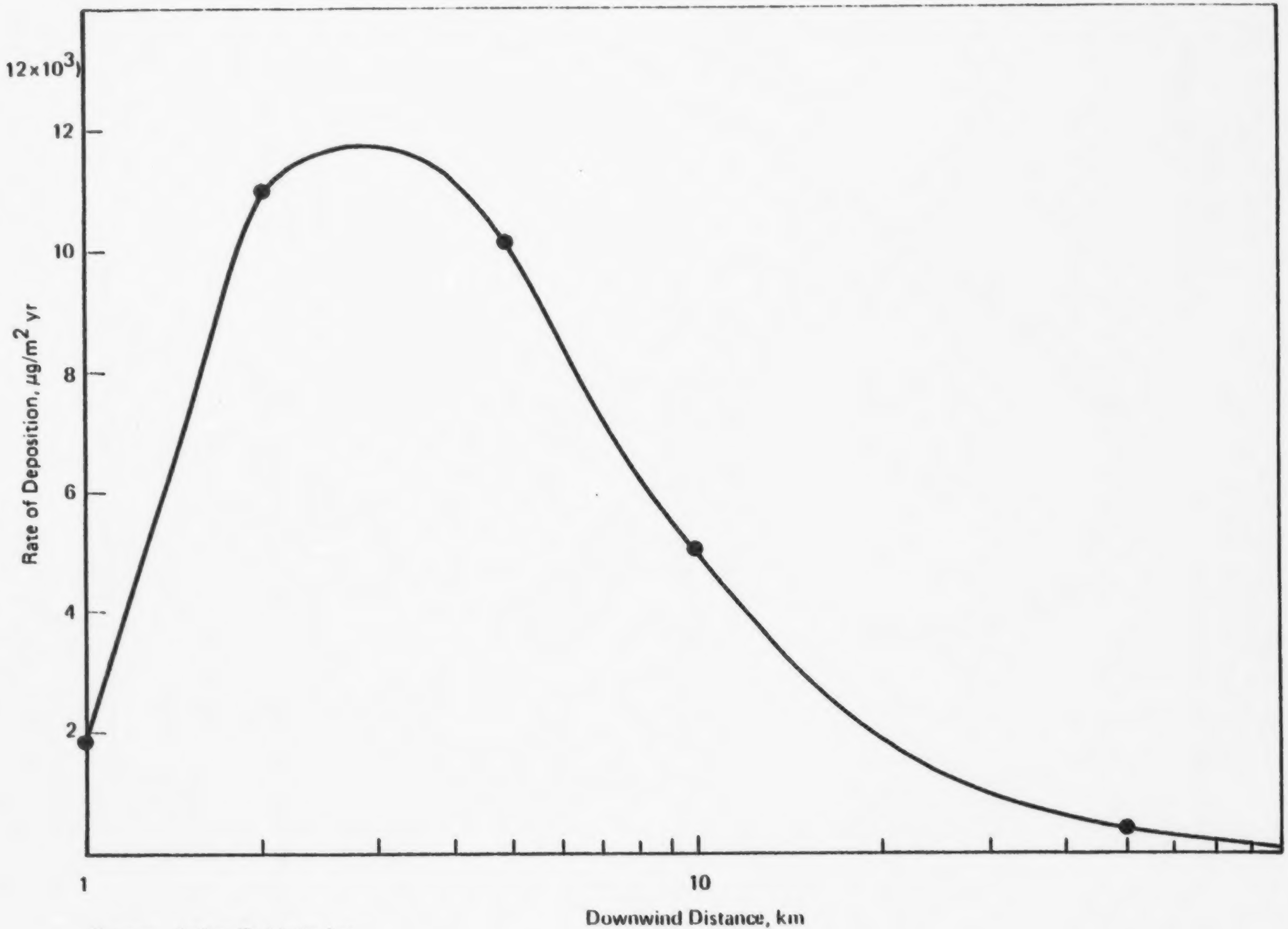
4.4.1 Introduction

Under special conditions, both natural and manmade, nickel may be present in soil at high enough concentrations to support significant nickel accumulation in plant tissues, possibly resulting in toxic effects. This is an important pathway to consider in terms of potential exposure of humans, wildlife, and plants themselves.



Source: Arthur D. Little, Inc.

FIGURE 4-3 AIRBORNE CONCENTRATION OF NICKEL AS A FUNCTION OF DOWNWIND DISTANCE



Source: Arthur D. Little, Inc.

FIGURE 4–4 GROUND LEVEL DEPOSITION OF NICKEL AS A FUNCTION OF DOWNWIND DISTANCE

Nickel is a normal constituent of both soil and plants. Concentrations reported as typical in soil range from 10 μg/g to 1000 μg/g and are dependent on various factors, including the constitution of the parent material, degree of weathering, age of soil, organic matter levels, and others (Allaway 1968). Certain soils, notably serpentine soils[1], have very high levels of nickel as well as other metals, often comparable to or higher than levels found in contaminated soil (e.g., near a smelter). Restricted growth of plants on these soils is partly attributed to nickel toxicity; however, other factors also contribute to the total toxicity, including high chromium levels, low molybdenum levels, and unbalanced magnesium-calcium ratios (Vanselow 1966).

Table 4-4 presents ranges of nickel concentrations in soil, both naturally occurring and associated with anthropogenic nickel sources. The highest anthropogenic levels reported were found in the immediate vicinity of a nickel smelter (<1 km). Sludge-amended soils have variable nickel concentrations, depending on the sludge source and application rate. The presence of nickel in super-phosphate fertilizers may also result in increased nickel levels in soil and plants (NAS 1975). Nickel levels in soil are discussed in more detail in Section 4.5 (Monitoring Data).

The concentration of nickel in soil which is important in regard to plants is the exchangeable fraction, not the total concentration (Vanselow 1966). Exchangeable nickel is extracted by a neutral normal ammonium acetate solution or acetic acid. The extractable concentration in soil is dependent on the availability of iron and manganese hydrous oxides and organic chelates (CAST 1976). Most measurements of nickel in soil are of total nickel[2] so are not particularly useful for comparison with effects of bioaccumulation levels in plants. The actual available concentration of nickel in total concentrations of 10 μg/g to 6000 μg/g in soil may only range from 1 μg/g to 70 μg/g (see Tables 4-4 and 4-5). There appears to be a good correlation between exchangeable Ni in soil and the Ni content in grasses (Soane and Saunder 1959).

The extractable fraction of nickel does not correlate well with plant tissue concentrations in general, however, due to wide species varability (Davis 1979). The reason for this may be that the extracted fraction is what is available to plants, not actually assimilated by them. Species differences in uptake and soil characteristics (pH, cation exchange capacity, organic content) influence the efficiency of uptake. Acidic extractants, such as acetic acid, may mask soil pH effects which are especially influential on bioaccumulation. Use of ammonium acetate solution as an extractant apparently does eliminate these analytical problems.

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[1] Natural soils containing high mineral levels, especially Mg and Si.

[2] Unless otherwise noted, all concentrations in Table 4-4 are for total nickel.

TABLE 4-4. NICKEL CONCENTRATIONS IN SELECTED SOIL TYPES

LOCATION OF SOIL	NICKEL CONCENTRATION	REFERENCE
Natural background levels (typical soil)	5-500 μg/g (typical) 40-100 μg/g (average) (exchangeable Ni usually <1 μg/g)	Vanselow (1966), Allaway (1968)
Natural background levels (serpentine soils)	400-6200 μg/g (exchangeable Ni 3-70 μg/g)	Vanselow (1966)
In vicinity of nickel smelter	≈300-500 μg/g (decreasing with distance from smelter)	Rutherford and Bray (1979)
By highway	≈2-8 μg/g (decreasing with distance from road)	Lagerwerff and Specht (1970)
In vicinity of copper smelter	1.05±0.2 μg/g (extractable) (within 0.5 km of source)	Beavington (1975)
Sludge-amended soils	2-50 μg/g 40 μg/g (mean)	Page (1974) U.S. EPA (1976)

TABLE 4-5. ACCUMULATION OF NICKEL IN CROPS GROWN ON SLUDGE-AMENDED SOIL

Soil and/or Sludge Ni Concentration	Crop Species	Ni Concentration in Crop (ug/g dry)	Reference
Total of 1260 kkg of sludge/ha over 19 years (66 kkg/ha/yr). Concentration in soil 8.1 ug/g dry matter.	Leek Beet tops Beet roots	7 (3.5 x control) 16.5 (5 x control) 13 (9 x control)	Le Riche (1968)
Nickel at 88 ug/g in sludge applied at 9.2 kg/ha to soil (lower than typical U.S. sludge levels).	Rape	9.2 (≈2 x control)	Andersson and Nilsson (1972)
Nickel applied in sludge at 42 kg/ha-165 kg/ha.	Corn	0.3-3.0 (leaf)	Clapp et al. (1976)
Nickel at 20 ug/g in sludge applied at 24 kkg/ha.	Various crops	0.8-76 (fruit, root) 1.8-6.2 (leaves)	Giordano and Mayer (1980)
Nickel at 560 ug/g in sludge applied at 20 and 60 kkg/ha—one-time application (Ni at 11 and 33 kg/ha).	Lettuce, Tomatoes, Radishes, Carrots	6-10; 3-7; 5-11; 11-18, respectively over 2 year period (in edible portion). Slightly higher than control.	Schauer et al. (1980)
Sludge applied to 2 types of soil (pH 5.7 and 7.5) in pots at 0-640 ug/g	Lettuce	1) Control: 4 2) Soil 5-80 ug/g: 6-23 (high pH) : 7-241 (low pH) 3) Soil 160-640 ug/g: 29-166 (high pH) : 345-1150 (low pH)	Mitchell et al. (1978)
	Wheat grain	1) Control <1 (high pH) 2) Soil 5-80 ug/g: 1 (high pH) : 1.7-64 (low pH) 3) Soil 160-640 ug/g: 5-50 (high pH) 119-247^a (low pH)	
Other Studies			
Garden in vicinity of copper smelter (Ni at ≈1.05 ug/g in soil).	Lettuce	2.7-6	Beavington (1975)

[a] No determination at 640 μg/g

Approximately 15% of POTW sludge is applied to cropland for soil amendment (U.S. EPA 1979). A large fraction of the nickel in water undergoing treatment is trapped in the sludge at concentrations of 12 mg/kg up to 8000 mg/kg (see Section 4.3.3 - POTWs). When digested sludge is first mixed with soil under laboratory conditions, the fraction of heavy metals (copper and zinc) available for uptake fluctuates significantly over the first few months. Although comparable data for nickel were not available, it is likely that nickel behaves similarly (Wollan and Beckett 1979). Following this initial period, the extractable concentration of both nickel and other metals stabilizes and remains steady for at least 2 years. The ratio of extractable/total nickel in the sludge-mixed soil is variable and appears to be dependent upon the sludge source and amount applied (Wollan and Beckett 1979). At this time, however, there is no standard formula to determine the fraction of nickel in sludge potentially available for plant uptake in order to calculate an upper limit for the sludge application rate to crops.

4.4.2 Nickel in Plants - Bioaccumulation

Nickel is a basic constituent of organic matter and is present at background levels (<µg/g) in plants growing on typical Ni-content soils (Vanselow 1966). Plants growing on serpentine soils have higher tissue levels than plants grown on typical soils. Serpentine soils are widely distributed throughout the United States. Of the total mass of nickel present in a relatively unpolluted forest ecosystem, approximately 2% to 5% was estimated to be contained in living biomass, with an additional 2% in soil organic matter (Heinrichs and Mayer 1980).

Plants growing on nickel-contaminated soils may accumulate the ion up to > 1000 µg/g in tissue. Certain species, especially leafy crops like lettuce, are likely to accumulate higher concentrations than other crops. Fruits and grains have not been observed to accumulate Ni preferentially.

Vanselow (1966) presents nickel levels in almost 40 species of crops grown predominantly under field conditions (no information is provided on whether the soil is sludge-amended or not). Almost all species had nickel levels at less than 4 µg/g, with the exception of a few grass or grass-like species (maximum 4000 µg/g in alyssum). Unfortunately background levels of nickel in the soil were not given. Table 4-5 presents levels of nickel reported in various crops grown on primarily sludge-amended soils. In most cases concentrations were less than 100 µg/g, depending on nickel levels, species, and soil characteristics. Soil pH, most notably, was a determinant in bioaccumulation with significant increases as the pH dropped below neutral. Therefore standard soil treatments, such as liming, would reduce nickel uptake by reducing the metal's solubility.

As discussed previously, it is difficult to predict plant tissue levels from soil concentrations of total nickel. Only a small fraction of the total amount present may be absorbed. Less than 0.4% of the nickel applied to soil in sludge at 3 kg/ha to 42 kg/ha ended up in the crops (Kelling et al. 1977).

4.4.3 Nickel in Animals

Nickel is believed to be an essential micronutrient for many organisms, but the exact amounts in which it is required have not yet been conclusively demonstrated. In terrestrial organisms (including animals and man), there are four routes of entry of nickel into the body. These include oral intake in food and drinking water; inhalation from the atmosphere; and absorption via the skin, a route of negligible quantitative significance and virtually unstudied in organisms other than laboratory animals and man. Ingestion and, to a much lesser extent, inhalation are the most important routes of uptake in non-human biota (NAS 1975). It has been shown in studies with cattle, laboratory animals, and humans that most of the nickel ingested via food remains unabsorbed within the gastrointestinal tract and is excreted in the feces and urine. Schroeder (1962) stated that there appeared to be a mechanism that limits the intestinal absorption of nickel in mammals. In laboratory animals it was found that inhaled nickel carbonyl was excreted primarily in the urine, to a lesser extent in the feces, and by the lungs themselves (NAS 1975).

4.4.4 Summary

Nickel accumulates in plants primarily through root uptake from soil. Natural background levels of < 1 μg/g are present in most plants. Crops growing on sludge-amended soil and near other nickel sources, however, accumulate higher levels, usually up to 4 μg/g. Soil pH is a very important factor in uptake; acidic soils support tissue accumulation levels of as much as an order of magnitude greater than alkaline soils. Lettuce, grasses, and grass-like plants have the highest reported tissue concentrations of nickel. The highest reported concentration was 1150 μg/g in lettuce grown in sludge-treated soil with nickel levels of 640 μg/g.

Information regarding the bioaccumulation and fate of nickel in terrestrial fauna is very limited. In mammals, the majority of nickel ingested (the most significant exposure pathway) is unabsorbed and excreted. Therefore, significant accumulation is not expected, even from ingestion of highly contaminated vegetation.

4.5 MONITORING DATA

4.5.1 Introduction

Monitoring data for nickel concentrations in the environment have been collected and analyzed for air, water, and soil. Data relating to concentrations in biota do not appear as readily available, although some information is available. This section presents in some detail data on nickel concentrations in ambient, effluent, and well waters; dissolved and suspended matters; sediment; air; soils; and biota.

4.5.2 Water

4.5.2.1 Ambient Waters

The range of nickel concentrations in ambient waters reported in the STORET Water Quality System is from 0 μg/l to 100 μg/l (U.S. EPA 1980). Table 4-6 presents the distribution of unremarked observations from 1970 to 1979.[1] With roughly an equal number of samples documented annually since 1973, the pattern depicts approximately a third of the observations in each of the following ranges, 0 to 1 μg/l, 1.1 to 10 and μg/l, and 10.1 to 100 μg/l.

Figure 4-5 shows nickel concentrations representing the 85th percentile from 1975 to 1981. The crossed and heaviest shadings represent areas with nickel concentrations exceeding 50 μg/l. The states of Pennsylvania, West Virginia, Illinois, and Ohio appear to have the highest concentrations of nickel overall, while several states in the southern, midwestern, and Rocky Mountain areas have scattered localized areas with nickel concentrations above 50 μg/l. In the eastern areas, higher nickel concentrations may be attributed to electroplating and iron and steel facilities, and in the western areas, to mining operations. Higher nickel concentrations in the scattered localized areas throughout the country may be attributed to numerous factors, such as localized environmental conditions.

Over time the location of higher nickel concentrations has moved around the country. In 1970, major basins with annual average nickel concentrations exceeding 100 μg/l included the Northeast, Lower Mississippi, and Lake Erie. In 1979, only one major basin had an annual average nickel concentration exceeding 100 μg/l, the Ohio River. Figure 4-6 presents the major river basins with annual average nickel concentrations exceeding 100 μg/l from 1970 to 1979.

In a study of water transport of heavy metal in the State of Tennessee, Perhac (1974) documented nickel in Joe Mill Creek at three locations as ranging from 7 to 9 μg/l. Metal concentrations in lake

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[1] Because of the volume of data on nickel in the STORET system, only unremarked data was retrieved for this analysis.

TABLE 4-6. STORET DATA ON DISTRIBUTION OF NICKEL CONCENTRATIONS IN U.S. AMBIENT WATERS FROM 1970 TO 1979[a]
(µg/l)

Year	Number of Unremarked Observations	Percent of Observations 0-1	1.1-10	10.1-100	100.1-1000	1000.1+
1970	1163	57	16	25	2	
1971	1377	40	8	44	8	
1972	2346	45	20	29	5	
1973	3867	41	22	32	4	
1974	3562	37	25	32	6	1
1975	4164	26	29	42	3	
1976	4292	28	31	38	3	
1977	4072	20	31	44	5	
1978	4109	21	25	47	4	3
1979	3095	16	38	37	5	5

[a] Retrieved July 22, 1980.

Source: U.S. EPA (1980)

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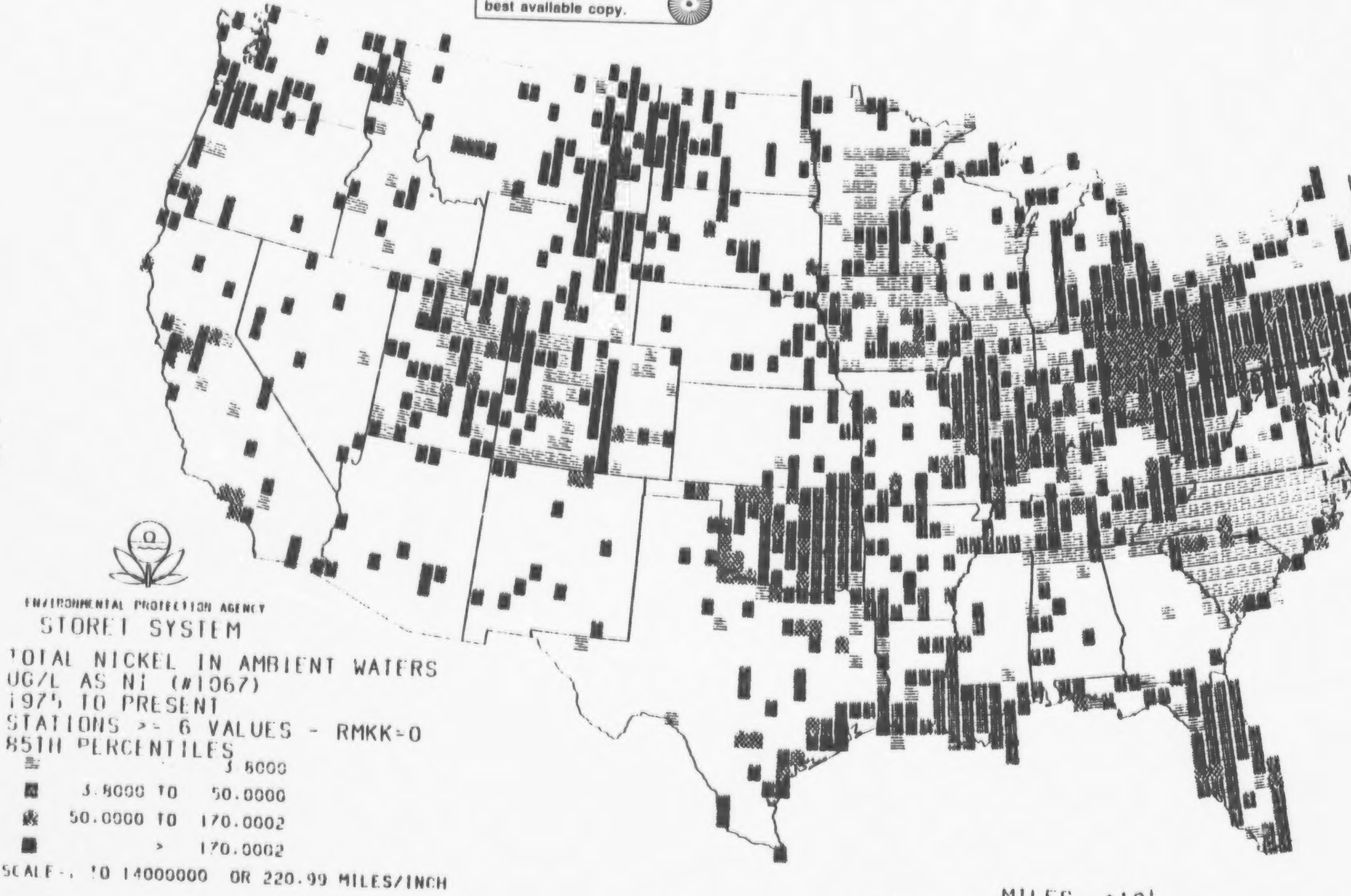
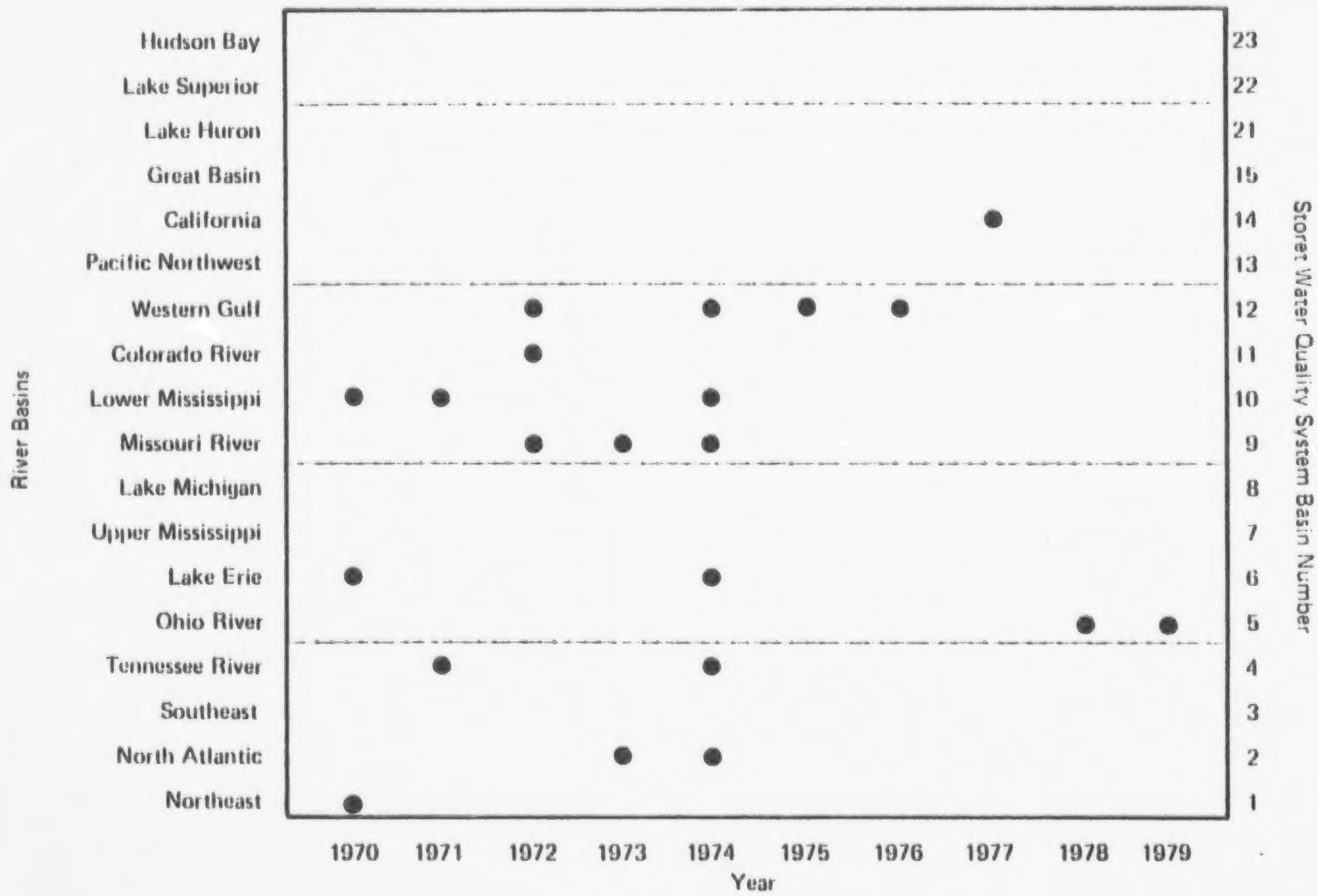

ENVIRONMENTAL PROTECTION AGENCY
STORET SYSTEM
TOTAL NICKEL IN AMBIENT WATERS
UG/L AS NI (#1067)
1975 TO PRESENT
STATIONS >= 6 VALUES - RMKK=0
85TH PERCENTILES
▤ 3.8000
▨ 3.8000 TO 50.0000
▩ 50.0000 TO 170.0002
■ > 170.0002
SCALE-, 1 TO 14000000 OR 220.99 MILES/INCH
MILES *10'
0.00
22.10
44.20
66.30
88.40

Source: U.S. EPA 1980.

FIGURE 4–5 NICKEL CONCENTRATIONS IN U.S. WATERS, 1971–1979 (μg/ℓ)
(Unremarked Values)



Source: U.S. EPA 1980.

FIGURE 4–6 MAJOR RIVER BASINS WITH ANNUAL AVERAGE NICKEL CONCENTRATIONS IN AMBIENT WATERS EXCEEDING 100 $\mu g/\ell$ – STORET DATA

surface water of the Adirondack region of New York State were examined by Williams et al. (1977) in the summer of 1975. Nickel concentrations ranged from 0.4 µg/l to 14.8 µg/l in the northern and southern portions of seven lakes. No trend was determined for nickel in the lakes, with the exception of Ticonderoga Bay of Lake Champlain where pollution from industrial wastes existed.

From a review of literature by Bowen (1979), concentrations of nickel in freshwater form a range of 0.02 µg/l to 27 µg/l, with a median of 0.5 µg/l; in sea water the range is 0.13 µg/l to 43 µg/l, with a mean of 0.12 µg/l.

4.5.2.2 Effluent Waters

The STORET system is one of the primary data bases for information regarding nickel in effluent waters. Since 1977, sampling of nickel in effluent waters has been recorded for the Northeast, North Atlantic, and Southeast basins. Table 4-7 shows concentrations of nickel in effluent waters for the three basins, along with a gross summary. The retrievals were of a general nature; neither industry nor plant specific data was analyzed. For the three areas combined, the maximum concentration is 400 µg/l, with a mean concentration of 47 µg/l. Overall, the Northeast has the highest concentrations of nickel in the effluent waters from year to year.

Samples of nickel were collected near a domestic sewage outfall in Central Puget Sound, Seattle, Washington (Schell and Nevissi 1977). Concentrations of nickel were found to be at or below open sea water values of 20 µg/l at three depths, up to 2 m, 50 m, and 100 m.

2.5.2.3 Well Waters

The STORET system serves as the primary data source relating to nickel concentrations in well water.

Nickel concentrations in well waters are fairly uniform across the country. In the Ohio River Basin, maximum concentrations of 31,200 and 31,700 µg/l were reported in 1978 and 1979, respectively. Typically, the maximum concentration of nickel in well waters did not exceed 50 µg/l and the average concentration centered around 10 µg/l; the average was below the Water Quality Criterion of 13.4 µg/l. Table 4-8 shows, by major basin, nickel concentrations in well waters from 1977 to 1979.

4.5.3 Dissolved and Suspended Matters

Water transport of heavy metals by particulate solids was examined by Perhac (1974), in eastern Tennessee. The concentration of metals in the particulates was documented as very high but the quantity of particulate matter was quite low.

TABLE 4-7. NICKEL CONCENTRATIONS IN EFFLUENT WATERS 1977-1979 - STORET DATA (ug/l)

Major River Basin	Number of Observations	Maximum	Minimum	Mean
Northeast				
1977	83	300	0.15	44
1978	79	400	0.12	65
1979	2	100	100	100
North Atlantic				
1977	26	240	3	41
1978	31	56	1	16
Southeast				
1977	2	52	5	29
1979	10	81	20	35
Gross Analysis	233	400	0.12	47

Retrieved July 22, 1980.

Source: U.S. EPA 1980

TABLE 4-8. NICKEL CONCENTRATIONS IN WELL WATERS, 1977-1979 - STORET DATA ($\mu g/l$)[a]

Major River Basin	Number of Observations	Concentrations Maximum	Concentrations Minimum	Concentrations Mean
North Atlantic	32	40	10	16
Southeast	11	177	0.00	29
Ohio River	59	31,700	5	8443
Lake Erie	1	5	5	5
Upper Mississippi	192	50	0.13	4
Missouri River	19	15	1	8
Pacific Northwest	7	21	2	6
Hudson Bay	25	10	1	3

[a] Retrieved July 22, 1980.

Source: U.S. EPA (1980)

Nickel concentrations in dissolved solids at six sampling sites ranged from 9000 µg/l to 45,000 µg/l. The nickel content in coarse particulates at the same sites ranged from 35,000 µg/l to 110,000 µg/l. The largest percentage of nickel was uncovered in dissolved solids as opposed to particulate solids, being at least 73% at five sampling sites (the sixth site was considerably lower).

Table 4-9 displays the documentation of nickel concentrations in dissolved and suspended matters, as reported from STORET, for most major basins from 1977 to 1979. For the nation as a whole, maximum and average nickel concentrations in dissolved matters are 1000 and 24 µg/l, and for suspended matters, 1400 and 13 µg/l.

4.5.4 Sediment

The transport of heavy metal in bottom sediments was examined in the waters of eastern Tennessee to define the distribution of heavy metals in a fluvial system (Perhac. 1974). Nickel was one of eight heavy metals measured in a stream located in an industrialized urban area, in a stream which flows over exposed carbonate rocks containing zinc minerals, and in a stream located in a rural non-mineralized area. The quantity of heavy metals in bottom sediment varied considerably from sample to sample. Detailed analysis of bottom sediment samples from Joe Mill Creek and the Tennessee River was conducted. Generally, the concentrations of nickel increased with decreasing grain size, as shown in Table 4-10.

Samples taken from bottom sediment in the Tennessee River near Knoxville indicate that more nickel was present than in Joe Mill Creek, possibly because of petroleum wastes from many diesel vessels using the river. In Joe Mill Creek, the nickel content in bottom sediment ranged from 20,000 µg/l to 64,000 µg/l, compared to the range of 39,000 µg/l to 109,000 µg/l in Tennessee River bottom sediment. The higher levels of nickel in bottom sediment did not have an impact on the concentrations of nickel in surface waters, which were low at both sites.

Knauer (1977) determined the immediate impact of a new Australian nickel refinery on sediment metal levels in Halifax and Cleveland Bays, Australia, which is discussed here as a basis for comparison. Slightly higher levels of nickel appeared in the Queensland Nickel outfall adjacent to the refinery than at either Halifax or Cleveland Bays. The average concentrations (µg/g dry weight) of nickel in surface and subsurface sediments (>10 cm) for Queensland Nickel was 14 and 12 µg/g, Halifax Bay 11 and 11 µg/g, and Cleveland Bay 9.3 and 8.8 µg/g. Supplemental laboratory experiments suggested that the future levels of nickel in sediment would increase as a direct result of the new nickel refinery.

TABLE 4-9. NICKEL CONCENTRATIONS IN DISSOLVED AND SUSPENDED MATTERS FROM MAJOR RIVER BASINS, 1977 to 1979 - STORET DATA (µg/l)

Major River Basins	Dissolved Matter			Suspended Matter		
	Observations	Maximum	Mean	Observations	Maximum	Mean
Northeast	35	35	2	31	11	1
North Atlantic	218	100	72	18	22	5
Southeast	387	470	69	99	36	4
Tennessee River	107	100	94	7	17	4
Ohio River	195	800	55	23	26	5
Lake Erie	861	1000	8	1	0	0
Upper Mississippi	175	83	14	127	50	15
Lake Michigan	24	290	31	11	7	2
Missouri River	380	22	3	193	440	19
Lower Mississippi	533	50	4	439	180	11
Colorado River	193	35	3	116	1400	39
Western Gulf	38	75	3	35	16	4
Pacific Northwest	30	6	0.7	25	26	4
California	80	200	56	30	50	8
Great Basin	261	200	11	18	8	3
Lake Huron	3	9	3	3	3	1
Lake Superior	5	1	0.4	5	2	0.8
GROSS ANALYSIS	3525	1000	24	1181	1400	13

Retrieved July 22, 1980.

Source: U.S. EPA (1980)

TABLE 4-10. NICKEL CONTENT IN BOTTOM SEDIMENT SAMPLES

	Nickel Content (mg/l)						
	Composite	Size Fraction (μ)					
Joe Mill Creek	Total	<0.2	0.2-2	2-5	5-50	50-100	>100
Sample 1	12-32	82	83	70	31	27	<30
Sample 2	12-31	108	87	75	28	27	<28
Sample 3	52	99	187	66	43	41	60
Tennessee River							
Sample 1	--	186	108	89	69	80	50
Sample 2	--	227	150	208	69	50	20
Sample 3	--	135	90	69	50	30	40
Sample 4	--	220	237	271	90	89	80

-- indicates not available

Source: Perhac (1974)

Concentrations of nickel were measured at several depths in sediment at various lakes of the Adirondack Mountain region of New York State (Williams, et al.). Nickel concentrations in surface and subsurface sediments (10 to 20 cm) were analyzed for seven lakes. Concentrations in surface sediments ranged from 0.2 μg/g to 5.0 μg/g and from 0.1 μg/g to 2.9 μg/g in subsurface sediment. Lakes with higher nickel concentrations were subject to pollution from industrial wastes.

Levels of organometallic nickel were determined in sediment by Nakamura and Kashimoto (1979). Heavy metals in crude oil reach sediment as a result of oil pollution in the sea environment. From three sediment samples taken in Osaka Port, the levels of organometallic nickel (dry matter) were 0.218 μg/g, 0.149 μg/g, and 0.180 μg/g.

Nickel in sediments has been documented by Bowen (1979) from literature as 225 μg/g in marine clay, 30 μg/g in marine carbonates, and mean levels of 68, 7, 9, and 52 μg/g in shale, limestone, sandstone, and sediment, respectively.

Nickel concentrations in sediment have been recorded in fourteen of the continental major basins. During the three-year period of 1977 to 1979, maximum concentrations of nickel in sediment ranged from 20 to 1200 μg/g and mean concentrations from 4 to 172 μg/g. These results are consistent with findings in the literature. Nickel concentrations in sediment are displayed in Table 4-11 for the reporting basins and in the United States. In general, nickel concentrations in sediment are two to three orders of magnitude higher than nickel concentrations in ambient waters. Figure 4-7 presents concentrations of nickel in sediment for the nation from 1971 to 1976. The heaviest shading represents concentrations exceeding 25 μg/g. Sampling since 1976 indicates basically the same conditions, with expansions to the western section of the country.

4.5.5 Air

4.5.5.1 Industrial Areas

Emission data with respect to nickel have been documented for several emission categories, including mining, metallurgical, fuel combustion, waste incineration, secondary metal industry, consumptive uses, and processing and utilization. Table 4-12 exhibits the emission factors for nickel from these industrial categories.

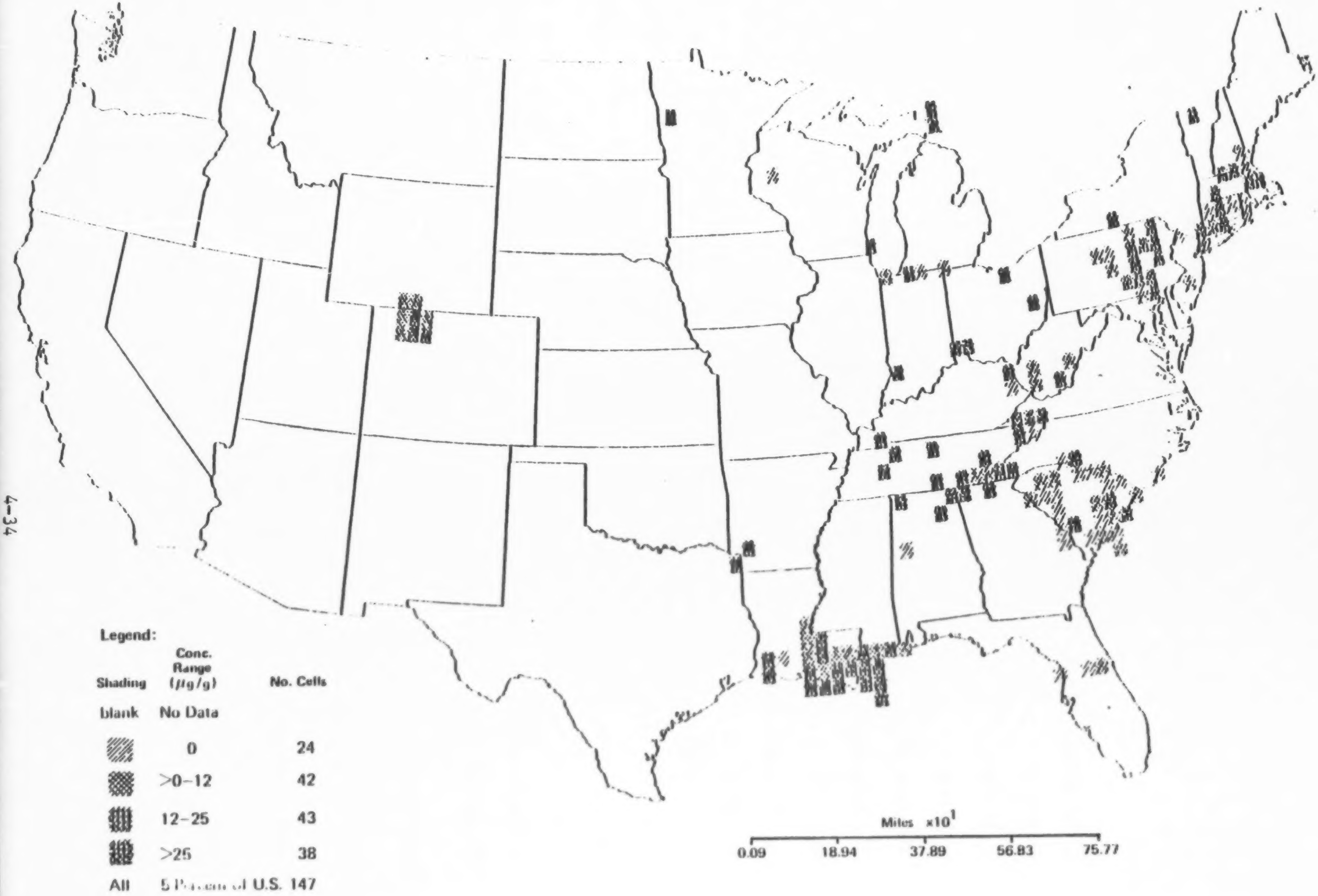
Other emissions of nickel have been documented (Schroeder 1962). Fly ash from residual fuel oil used in power plants and in heating large office buildings, apartments, and schools has 1.8 to 10% nickel oxide. Fly ash crude oil used in the facilities contained 55 μg/g, and asphaltene fraction 245 μg/g. Particulates from municipal incinerators in Milwaukee have 1 to 10% nickel.

TABLE 4-11. NICKEL CONCENTRATIONS IN SEDIMENT, 1977-1979 - STORET DATA[a] (μg/g)

Major River Basins	Number of Observations	Concentrations Maximum	Minimum	Mean
Northeast	58	200	5	18
North Atlantic	69	360	1	29
Southeast	172	80	7	12
Tennessee River	10	39	7	16
Ohio River	22	50	10	24
Lake Erie	247	290	1	37
Upper Mississippi	4	20	5	11
Lake Michigan	22	1200	1	172
Missouri River	33	120	0.00	18
Lower Mississippi	37	40	0.00	14
Colorado River	15	20	0.00	4
Western Gulf	117	68	0.5	14
Pacific Northwest	27	238	4	47
Lake Huron	6	23	5	15
GROSS ANALYSIS	839	1200	0.00	27

[a] Retrieved July 22, 1980.

Source: U.S. EPA (1980)


Legend:
Shading
Conc. Range ($\mu g/g$)
No. Cells
blank No Data
▨ 0 24
▦ >0–12 42
▥ 12–25 43
▩ >25 38
All 5 Percent of U.S. 147
Miles x10^1
0.09
18.94
37.89
56.83
75.77

Source: U.S. EPA 1980.

FIGURE 4–7 NICKEL LEVELS IN SEDIMENT, 1971–1976

TABLE 4-12. EMISSION FACTORS FOR NICKEL FROM INDUSTRIAL SOURCES

SOURCE	EMISSION FACTOR
Mining and Metallurgical	9 kg/10^3 kg of nickel produced
Processing of Nickel	5 kg/10^3 kg of nickel charged
Stainless steel	0.3 kg/10^3 kg of stainless steel produced
Nickel alloy steel	5 kg/10^3 kg of nickel charged
Iron and steel scrap	0.0008 kg/10^3 kg of steel and iron
Nickel alloys	1 kg/10^3 kg of nickel charged
Copper base alloys	1 kg/10^3 kg of nickel charged
Electrical alloys	1 kg/10^3 kg of nickel charged
Cast iron	10 kg/10^3 kg of nickel charged
Batteries	4 kg/10^3 kg of nickel processed
Cement Plants: Dry Process	
Kiln	200 kg/10^3 kg of feed
Feed to raw mill	5 kg/10^3 kg of feed
Air separator after raw mill	0.5 kg/10^3 kg of feed
Raw mill	0.3 kg/10^3 kg of feed
Air separator after finish mill	0.2 kg/10^3 kg of feed
Feed to finish mill	5 kg/10^3 kg of feed
Cement Plants: Wet Process	
Kiln	100-1000 kg/10^3 kg of feed
Clinker cooler (exit from baghouse)	2 kg/10^3 kg of feed
Clinker cooler (exit from electrostatic precipitator)	50 kg/10^3 kg of feed
Clinker cooler (exit from two baghouses)	100 kg/10^3 kg of feed
Finishing mill after air separator	2 kg/10^3 kg of feed
Coal-fired boilers	0.2 kg/10^3 kg coal burned
Power Plant Study	
South Carolina	0.0003 (0.0002 to 0.0005) kg/10^3 kg coal burned
Michigan	0.0003 (0.0002 to 0.0005) kg/10^3 kg coal burned
Illinois	0.0002 kg/10^3 kg coal burned
Kansas	0.0003 (0.0002 to 0.0005) kg/10^3 kg coal burned
Fuel Combustion Oil	
U.S. Crude Oil:	
Texas	0.002 (0.001 to 0.006) kg/10^3 liters crude oil
Louisiana	0.002 kg/10^3 liters
Kansas	0.005 kg/10^3 liters
Wyoming	0.002 kg/10^3 liters
California	0.05 kg/10^3 liters
Alaska	0.01 kg/10^3 liters
Average for U.S. crude oils	0.01 kg/10^3 liters
Average for imported crude oils	0.009 kg/10^3 liters
Foreign crude oils	
Monagas crude, Venezuela	0.04 kg/10^3 liters
Crude oil, Venezuela	0.006 kg/10^3 liters
Nigerian crude oil	0.007 kg/10^3 liters
Jobo crude, Puerto Ordaz, Venezuela	0.05 kg/10^3 liters
Aguasay crude oils, Venezuela	0.002 kg/10^3 liters
Average for foreign crude oils	0.02 kg/10^3 liters
Foreign Residual Oils	
#6 fuel oil, Virgin Islands	0.03 kg/10^3 liters
#6 fuel oil, Venezuela	0.04 (0.004 to 0.06) kg/10^3 liters
#6 fuel oil, Aruba, N.A.	0.03 kg/10^3 liters
#6 fuel oil, St. Croix, VI	0.01 kg/10^3 liters
#6 fuel oil, El Palito, Venezuela	0.06 kg/10^3 liters
#6 fuel oil, Puerto La Cruz, Venezuela	0.05 kg/10^3 liters
#6 fuel oil, Spain	0.02 kg/10^3 liters
#6 fuel oil, Trinidad	0.03 kg/10^3 liters
#6 fuel oil, Canada	0.02 kg/10^3 liters
Average for foreign crude oils	0.03 (0.004 to 0.06) kg/10^3 liters
U.S. Boilers	
Residential units	0.00005 to 0.00006 kg/10^3 liters
Commercial units #6	0.01 kg/10^3 liters
Commercial units #5	0.007 kg/10^3 liters
Commercial units #4	0.006 kg/10^3 liters
Sewage Sludge Incinerators	
Multiple hearth	0.002 kg/10^3 kg of solid waste incinerated
Fluidized bed	0.0002 kg/10^3 kg of solid waste incinerated
Municipal Incinerator	
Refuse only	0.02 kg/10^3 kg of solid waste incinerated
Refuse and sludge	0.003 kg/10^3 kg of solid waste incinerated
Lubricating Oil	0.008 kg/10^3 liters of lubricating oil

Source: Anderson (1973)

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Sullivan (1969) documented concentrations of nickel near the Alloy Products Division of the International Nickel Company, Inc. in Huntington, West Virginia, as 1.2 $\mu g/m^3$. Concentrations at six other sampling stations in the Ironton-Ashland-Huntington Valley were lower, at 0.04 $\mu g/m^3$.

In the heavily industrialized city of Glasgow, Scotland sites were selected to construct a comprehensive view of the atmospheric conditions with respect to airborne metallic pollutants (McDonald and Duncan 1978). Sample sites were located in residential areas, some distance from polluting sources, in the vicinity of shipbuilding, iron and steel, and coal-burning power station operations, and in close proximity to main thoroughfares. The range and mean values of 11 metals, including nickel, were documented, and compared with values reported for other urban areas. In general, mean values were in agreement with those for other areas. However, the mean value (128 ng/m^3) reported for nickel, in particular, was higher by a factor of 2 than values reported in Chicago (60 ng/m^3) and Galmorgan, Wales (65.6 ng/m^3), and higher by a factor of 12 when compared to results from 50 stations in Texas (10 ng/m^3).

In Wollongong, Australia, significant correlations were found between distance from copper smelter and heavy metal contamination of vegetables and soil in domestic gardens around the smelting complex (Beavington 1975). Specifically, in a garden only 150 meters from the main chimney 6 $\mu g/g$ of nickel was reported in the leaf of a mature flowering plant. Twenty-one samples of leaf vegetables were collected from 17 gardens, along with soil samples up to 10 cm. Mean levels of nickel calculated at dry matter weight for lettuce, other leaf vegetables, chilies, and soil were 2.7 $\mu g/g$, 5.0 $\mu g/g$, 0.9 $\mu g/g$, and 1.05 $\mu g/g$, respectively.

4.5.5.2 Urban Areas

The presence and concentrations of several airborne metallic pollutants were surveyed in 58 cities (Schroeder 1962). Nickel was detected in 56 of the cities, forming a range of 1 ng/m^3 to 118 ng/m^3. The cities polluted heavily with airborne nickel, with concentrations ranging from 30 ng/m^3 to 120 ng/m^3, include New York City and Rochester, New York; Bayonne, New Jersey; Portland, Oregon; Somerville, Massachusetts; New Haven, Hartford, and Bridgeport, Connecticut; Bakersfield, Burbank, and San Bernardino, California; and Baltimore, Maryland.

Seasonal changes exhibited variations in mean nickel concentrations in ten cities. During colder months, the mean concentration of nickel was documented at 44 ng/m^3 compared to 26 ng/m^3 in warmer months. This is attributed to an increased use of petroleum and coal in the colder months.

The dry deposition of toxic trace metals was studied in New York City beginning in 1972 (Kleinman *et al*. 1977). Weekly samples of suspended particulates and monthly fallout samples were collected for 12 metal elements by atomic-absorption spectrophotometry at four locations. The results of average nickel dustfall and ranges of monthly nickel concentrations for three stations were:

Station Location	mg/cm^2·month Average	mg/cm^2·month Range
Bronx	400	14-2500
Lower Manhattan	400	33-3200
Midtown Manhattan	300	64-1900

Sullivan (1969) documented concentrations of nickel in the urban atmosphere ranging to a maximum of 690 ng/m^3 with an average of 32 ng/m^3 in a 1964 national sampling survey.

4.5.5.3 Rural Areas

Documentation of nickel concentration in the rural atmosphere is very limited. A survey of airborne metallic pollutants, including nickel, was conducted in 29 non-urban areas (Schroeder 1971). In 28 of the 29 areas, concentrations of nickel in the air were documented as a range of 6 ng/m^3 to 12 ng/m^3. In the 29th area, it was undetected.

4.5.6 Soils, Rocks, and Plants

About 0.008% of the earth's crust is nickel, with the largest portion, approximately 0.01 %, in igneous rocks (Nielsen *et al*. no date) Of the igneous rocks in the lithosphere, the ultramafic rocks are abundant in nickel -- 140 µg/g in gabbro to an average of 2000 µg/g in peridotite. Diorite contains roughly 40 µg/g of nickel and granite rocks 8 µg/g. An average of approximately 50 µg/g of nickel is found in sedimentary rocks, shale, and carbonate rocks.

In plant tops, the average range of nickel concentrations is 0.05 µg/g to 5 µg/g, dry weight. Nickel concentrations in plants materials used as food are shown in Table 4-13.

Contamination of roadside soil and vegetation near roadways used by motor vehicles was studied (Lagerwerff and Specht 1970). Sites were selected on level areas near four heavily trafficked roads--U.S. 1 at Beltsville, MD, Washington-Baltimore Parkway at Bladensburg, MD, I-29 at Platte City, MO, and Seymour Road north of Cincinnati, OH. Soil samples were collected at distances of 8, 16, and 32 m from traffic and at depths of up to 5, 10, and 15 cm. Results (shown in Table 4-14) indicate that concentrations of nickel in soil and vegetation decrease with distance from traffic and with depth.

TABLE 4-13. NICKEL CONCENTRATIONS IN FOODSTUFF

ITEM	CONCENTRATION	
	Wet Weight (μg/1)	Dry Weight (μg/g)
GRAINS		
Wheat	0.16-0.74	0.34-35
Bread, whole wheat	1.33	-
Cereals	0.13-3.00	-
Oats	1.71-2.60	0.45
Rice	0.30-1.80[a]	0.02[b]
VEGETABLES AND FRUIT		
Potatoes	0.56	0.08-0.37
Peas	0.30-1.66	2.00-2.25
Beans	0.17-2.59	0.59
Celery, fresh	0.37	-
Swiss chard, Chicory, Spinach Escarole	0.27-0.71	2.40
Lettuce, head	0.14	1.51
Lettuce, organic	1.14	-
Cabbage	0.14-0.32	3.30
Watercress	-	0.13
Tomatoes	0.02	0.01-0.15
Tomato Juice, canned	0.05	-
Broccoli	0.33	-
Carrots	-	0.30
Mushrooms	-	3.50
Onions	-	0.16
Apples	0.08	-
Bananas	0.34	-
Pears	0.20	0.90
Figs	-	1.20
Plums	-	0.90
Apricots	-	0.64
Oranges	-	0.16

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[a] Rice sampled includes polished, unpolished, and puffed.

[b] Polished rice.

Source: Nielson _et_ _al_. (no date).

TABLE 4-14. CONTAMINATION BY NICKEL OF ROADSIDE SOIL AND VEGETATION

Site	Meters From Road	Nickel in Grass (µg/g - dry weight)	Soil Profile Layer, cm (µg/g - dry weight) 0 - 5	0 - 10	10 - 15
U.S. 1 at Beltsville, MD					
	8	5.0	4.7	1.00	0.81
	16	3.8	2.4	0.90	0.60
	32	2.8	2.2	0.62	0.59
Washington-Baltimore Parkway at Bladensburg, MD					
	8	3.8	7.4	5.6	1.40
	16	2.5	4.4	1.6	0.79
	32	1.3	2.4	1.2	0.57

Source: Lagerwerff and Specht (1970)

In a review of literature, Bowen (1979) documented the median and range of nickel in soils at 50 µg/g and 2 to 750 µg/g, respectively. Documentation for nickel levels in minor sedimentary rocks (in µg/g) includes: manganese modules - 4900; phosphorites - <2 - 1000; petroleum - 10; and coal - 10 (mean) and 1-80 (range).

4.5.7 Biota

Documentation of nickel concentrations in biota in the STORET system reports maximum values ranging from 3 µg/g to 35 µg/g (dry weight) for shellfish and mean values 0.71 µg/g to 8 µg/g. Maximum concentrations in fish tissue range from 0.13 µg/g to 27 µg/g (wet weight) and mean concentrations from 0.11 µg/g to 3 µg/g. Concentrations of nickel in shellfish and fish tissue for major river basins are presented in Table 4-15.

Heavy metals in crude oil are frequently a source of contamination for marine products as oil pollution in the sea environment occurs. Nakamura and Kashimoto (1979) determined the levels of organometallic nickel in the hexane extracts of marine products from Japan. Table 4-16 exhibits the levels of organometallic nickel in marine products; the highest level of organometallic nickel appears in Turban shell intestine (0.063 µg/g) at Ishikawa, Japan.

4.5.8 Summary

Nickel has been detected in ambient surface waters of the United States at concentrations varying from <1 µg/g to 100 µg/l, with approximately two-thirds of the detections in the range of <1 µg/l to 10.0 µg/l. Ambient concentrations exceeding 100.0 µg/l have occurred at different times in various major river basins throughout the country, although most recently (1978, 1979) the Ohio River Basin has consistently had higher levels of nickel. The mean concentration of nickel in well waters is 10 µg/l, which is below the established human health criterion level for waters of 13.4 µg/l. However, higher levels of nickel were detected in well waters within the Ohio River Basin in 1978 and 1979. In stream sediments, the concentration of nickel tends to increase as sediment grain size decreases. More significantly, however, the nickel concentration in stream sediment increases greatly in areas near industrial discharges. Nickel occurs in air at concentrations up to an order of magnitude higher in urban and industrialized areas (1 to 690 ng/m^3) than in rural areas (6 to 12 ng/m^3).

Although nickel occurs naturally in the earth's crust and can be found at low concentrations in all of the environmental media, the highest concentrations detected in air, water, suspended sediments, and plants tend to be associated with industrial and urban activities. Concentrations of nickel in the environment are summarized in Table 4-17 from the primary data sources detailed in this section.

TABLE 4-15. CONCENTRATIONS OF NICKEL IN SHELLFISH AND FISH TISSUE[a]

(μg/g)

	SHELLFISH			FISH TISSUE		
	dry weight			wet weight		
MAJOR BASIN	# Obs.	Max.	Mean	# Obs.	Max.	Mean
Northeast	17	35	8	524	27	0.70
North Atlantic	32	4	2	218	6	0.32
Southeast	-[b]	-	-	8	1	0.57
Ohio River	-	-	-	42	10	2.00
Lake Erie	-	-	-	110	8	0.45
Upper Mississippi	-	-	-	9	0.13	0.11
Lake Michigan	-	-	-	140	0.50	0.26
Missouri River	-	-	-	11	0.43	0.18
Lower Mississippi	-	-	-	5	13	3
Colorado River	-	-	-	17	2	2
Western Gulf	23	7	3	8	10	3
Pacific Northwest	19	3	0.71	45	5	1
California	13	4	2	21	5	1
Great Basin				2	5	3
Lake Huron				142	3	0.41
Lake Superior				140	0.50	0.14
Alaska				6	1	0.58
Hawaii				18	8	1
GROSS ANALYSIS	104	35	3	1466	27	0.59

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[a] Retrieved July 22, 1980.

[b] Major basins without entries (shown with -) indicate no reported detections.

Source: U.S. EPA (1980)

TABLE 4-16. ORGANOMETALLIC NICKEL IN THE HEXANE EXTRACTS OF MARINE PRODUCTS FROM JAPAN

Marine Product	Source	Organometallic Nickel (μg/g)
Clam (Meretrix)	Ehime	0.010
	Ehime	0.005
	Kyusyu	0.003
	Korea	0.001
Short-necked clams (Tapes)	Mie	0.004
	Shizuoka	0.004
Corbicula (Corbicula)	Mie	0.003
	Shimane	<0.001
Turban shell (Turbo)	Ishikawa (shellfish)	0.017
	Ishikawa (intestine)	0.063
	Yamaguchi	0.017
Scallop (Pecten)	Aomori	0.008
	Aomori	0.004
Ear shell (Haliotis)	Tokushima	0.014
Ark shell (Arca)	Mie	0.019
Oyster (Crassostrea)	Hiroshima	0.003
	Hiroshima	0.027
	Hiroshima	0.005
	Hiroshima	0.016
Ceila stearnsii	Osaka	0.013

Source: Nakamura and Kashimoto (1979)

TABLE 4-17. CONCENTRATIONS OF NICKEL IN THE ENVIRONMENT

Media/Biota	Nickel Concentration
Ambient waters	0 to 100 µg/l, typically
Well waters	50 µg/l - maximum; 10 µg/l - mean, typically
Effluent waters	400 µg/l - maximum; 47 µg/l - mean
Sediment	1200 µg/g - maximum; 27 µg/g - mean
Dissolved matter	1000 µg/l - maximum; 24 µg/l - mean
Suspended matter	1400 µg/l - maximum; 13 µg/l - mean
Urban Atmosphere	1 to 690 ng/m^3
Rural Atmosphere	0.6 to 12 ng/m^3
Soils	0.57 to 7.40 µg/g (dry weight)
Rocks	2 to 750 µg/g
Plants (tops)	0.05 to 5 µg/g (dry weight)
Biota	
Shellfish	35 µg/g - maximum; 3 µg/g - mean (dry weight)
Fish Tissue	27 µg/g - maximum; 0.59 µg/g - mean (wet weight)

Note: These nickel concentrations provide a range of values that were discussed in the text of this chapter.

4.6 SUMMARY

Two important conclusions can be reached from the information on environmental fate, biotic fate, and monitoring presented in this chapter. First, low, natural background levels of nickel are present in all parts of the environment. Second, elevated concentrations of nickel appear to be fairly restricted to localized areas which are associated with industrial activity and the urban environment, particularly in sediments.

Physically, chemically, and biologically degrading processes cause nickel to be eroded and deposited in waters (ambient, effluent, and well), stream sediments, soils, air, and biota. Generally, these concentrations are quite low. Typical ambient and well waters contain nickel in the range of 5.0 to 10.0 ug/l and effluent waters have an average of 47 ug/l nickel. Sediments and dissolved and suspended stream matter have mean concentrations of nickel between 13 ug/l and 27 ug/l. Soils have concentrations ranging from 0.57 ug/g to 7.40 ug/g, with rocks somewhat higher. Plant levels are commonly below 1.0 ug/g. The background levels of nickel in the non-urban atmosphere are generally between 0.6 ng/m^3 and 12 ng/m^3. These levels remain consistently low throughout most of the natural environment.

There are a number of industrial and urban activities utilizing large quantities of materials which contain nickel. Fossil fuels are possibly the most significant natural resource or product used in the United States which contain nickel and consequently release large quantities of nickel to the atmosphere. The activities associated with the use of petroleum and coal directly and indirectly affect the nickel concentration in all of the environmental media through processes such as fallout, runoff, and plant uptake. There are other industrial and urban activities which release nickel to the environment, including the manufacture of cement, alloys, and iron and steel; sewage treatment and sludge incineration; and municipal incineration, particularly of nickel-bearing materials. It is in locations where these activities are intensified that the nickel concentrations become elevated.

Because a major portion of the releases are atmospheric, air becomes the environmental media with the highest initial concentrations of nickel. The other media are indirectly affected by atmospheric transport of nickel and consequently areas experiencing high atmospheric release of nickel are likely to experience high nickel concentrations in the surrounding soil, water, and vegetation.

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5.0 EFFECTS AND EXPOSURE -- HUMANS

This chapter discusses the human effects of exposure which have been studied, considers the established water quality criterion for humans, and presents dose-response extrapolations. The routes of exposure, by inhalation and ingestion and through percutaneous (dermal) exposure, are identified and quantified within the limits of the available data.

5.1 EFFECTS

5.1.1 Introduction

Nickel is thought to be an essential micronutrient since it nearly satisfies certain criteria for essentiality of trace elements. It appears, however, that no human disease states have been attributed to a nickel deficiency and experiments in animals support this conclusion. It seems quite unlikely that nickel deficiency could be a problem in human nutrition since its presence in the environment and diet is so ubiquitous. The NAS monograph (1975) discusses the essentiality of nickel in considerable detail.

Of far greater concern is the determination of levels of nickel exposure, by various routes, that are hazardous to human health. This is a particularly difficult task. While the "background" level of exposure to nickel through ingestion, inhalation, and skin contact has not been shown to be particularly hazardous, certain nickel compounds, especially nickel carbonyl, are clearly toxic. Most nickel compounds are toxic only at elevated doses via routes of entry to the body that permit high concentrations of nickel to be acheived at the cellular or, more importantly, at the subcellular level.

The crucial consideration for assessing the risk of nickel toxicity is whether or not nickel can be absorbed and then reach the susceptible sites in the organism. This depends on the exposure route and the physicochemical form of the nickel. It can be understood then that nickel carbonyl is especially toxic because its combination of volatility, lipid solubility, and chemical stability permit rapid absorption by most routes into the organism, and subsequent wide extracellular and intracellular distribution. Intracellular decomposition and oxidation to Ni^{++} exposes sensitive subcellular processes to nickel ion. Thus, nickel carbonyl is a near ideal carrier for nickel, circumventing most of the protective mechanisms and barriers of the body. In contrast, orally ingested nickel salts have low toxicity because they are poorly absorbed and that which is absorbed is rapidly excreted from the body. High levels of nickel in the diet or drinking water of experimental animals are tolerated with minimal effects.

The major area of concern is toxicity from inhalation of nickel compounds. A number of studies and several recent reviews have indicated that nickel-refinery workers are at increased risk of developing respiratory tract cancer. The role of nickel in the development of respiratory tract cancer is not clear, however, because these workers were also co-exposed to other suspected carcinogens (e.g., asbestos and polycyclic aromatic hydrocarbons). Also, the risk to nickel workers of developing respiratory tract cancer has declined because of greatly improved industrial hygiene which has reduced exposure to most if not all of the toxic and carcinogenic compounds. The use of retrospective epidemiological data to compute risk in terms of a dose-response relationship is virtually impossible because little or no quantification or speciation of the various nickel compounds is available.

Animal studies indicate that nickel carbonyl and nickel subsulfide are carcinogenic by the inhalation route. These and some other nickel compounds cause adverse lung pathology and have been shown to alter lung "cleansing" processes, such as muco-ciliary clearance and alveolar macrophage activity. *In vitro* assays tend to support the *in vivo* carcinogenicity results for certain nickel compounds.

Other areas of concern to the risk assessment are discussed in this section. Briefly, it has been reported that nickel carbonyl was found to be both teratogenic and fetotoxic in animal studies; high levels of nickel in drinking water or diet had adverse effects on neonates (newbornes) in animal studies; and nickel contact dermatitis is prevalent in humans but probably not life-threatening.

5.1.2 Pharmacokinetics

The major routes of exposure of man to nickel are via ingestion (food and water) and inhalation. Parenteral absorption (intravenous, intraperitoneal, subcutaneous, etc.) is not of importance in human exposure except, possibly, in the case of internal metal prostheses. Percutaneous absorption is minimal, but is important in connection with nickel allergy.

The extent and rate of absorption by any route varies widely with the physicochemical form of nickel. Variable lipid and water solubilities, chemical stability of the specific compounds, and their variable tendency to interact with other molecules *in vivo* practically preclude any useful generalizations about nickel absorption unless the chemical form of the nickel is specified. These considerations must be taken into account again when evaluating bio-distribution, metabolism, and elimination from the body.

5.1.2.1 Absorption

Ingestion of nickel is on the order of 500 μg/day in humans and almost all of this is excreted in the feces without being absorbed. According to several studies cited in the EPA criterion document (U.S. EPA 1979), 1 to 10% of dietary nickel is absorbed. Even when the Ni ion was intubated in a dilute acidic solution such that interaction with foodstuffs was largely avoided, only 3 to 6% of the dose was absorbed, regardless of the size of the dose (Ho and Furst 1973).

Horak and Sunderman (1973) found that fecal excretion of nickel by healthy human subjects was on average 100 times greater than urinary excretion. Thus, fecal excretion can be used as a measure of nickel ingestion.

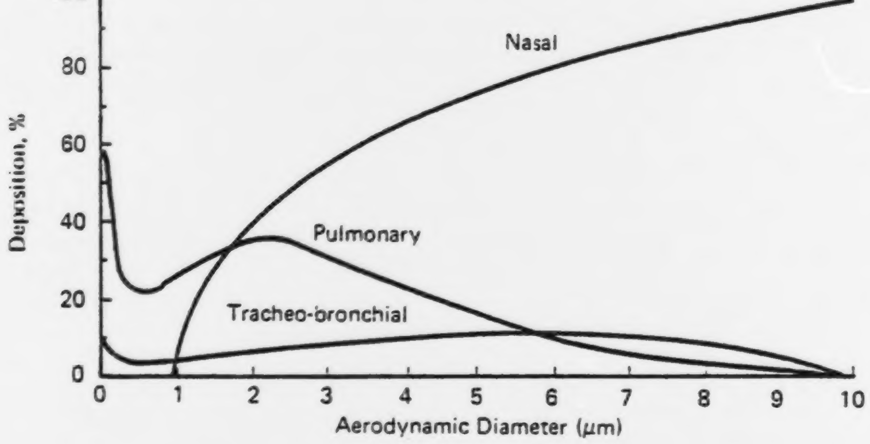
Distribution and metabolism studies indicate that absorbed nickel (Ni^{++}) is primarily excreted in the urine not into the bile and consequently the feces (Onkelinx et al. 1973); thus, it can be concluded that inorganic nickel compounds as are found in food and water are not absorbed to a significant extent and that entero-hepatic circulation does not explain fecal excretion of ingested nickel.

Inhalation is the most important route of exposure to nickel compounds from the standpoint of adverse health effects. The respiratory tract is both a point of entry to the rest of the body for toxic air pollutants and a site of toxic response. Typically, soluble aerosols and gases can pass through the lung epithelium into the blood in which they are transported throughout the body. Insoluble particulates tend to be deposited on the epithelium along the respiratory tract and may be retained in the lung for a much longer time. Whether or not a compound passes through or is retained by the lung markedly affects the nature of the effects.

The International Radiological Protection Commission Task Group on Lung Dynamics (IRPC 1966) has formulated detailed deposition and clearance models for inhaled particles. Deposition of the particles along the respiratory tract depends on particle size, density, hygroscopic properties, breathing rate, and whether breathing is via mouth or nose. Figure 5-1 and 5-2 indicate the predicted deposition in three respiratory tract zones as a function of aerodynamic diameter (unit density assumed) and at two breathing rates. Figure 5-1 indicates that at near resting breathing rates very small particles (~0.5 μm) are retained to a minimal degree. It is known, however, that these small particles penetrate farthest into the small airways and alveoli of the lung. Larger particles tend to deposit in the upper respiratory tract, especially the nasal passages. During mouth breathing, a greater fraction of inhaled particles are deposited in the lungs, although large particles are still deposited in the mouth and oropharynix (IRPC 1966).

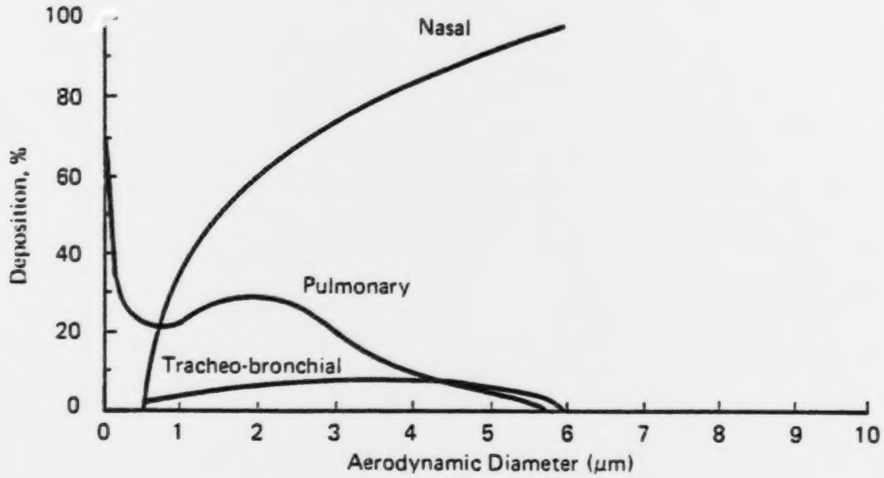
Clearance of particles from the lung depends on many factors including aqueous solubility, depth of penetration into the respiratory tree, and interaction of the particles with the tissue. Clearance mechanisms include dissolution, muco-ciliary transport, and endocytosis.

Experimental work on the absorption of nickel compounds via inhalation has been done almost exclusively in animals. Interpretations with respect to human inhalation are not straightforward. There are significant differences in breathing dynamics between humans and laboratory rodents. For example, rats and mice are nose breathers exclusively, while breathing in humans is through both nose and mouth. However, these experiments are illustrative of the variability in absorption, retention, and clearance of the different nickel compounds.



Source: IRPC (1966).

FIGURE 5–1 DEPOSITION AS A FUNCTION OF PARTICLE SIZE FOR 15 RESPIRATIONS/MINUTE, 750 cm^3 TIDAL VOLUME



Source: IRPC (1966).

FIGURE 5–2 DEPOSITION AS A FUNCTION OF PARTICLE SIZE FOR 15 RESPIRATIONS/MINUTE, 2150 cm^3 TIDAL VOLUME

Wehner and Craig (1972) exposed Syrian golden hamsters to nickel oxide (NiO) or cobalt oxide (CoO) dust in concentrations ranging from 2 μg/l to 160 μg/l (mg/m^3), having particle sizes of 1 to 2.5 μm (mass median aerodynamic diameter). Approximately 20% of the inhaled dose of NiO was deposited in the lung as determined after acute, 3 week subacute, or 3 month subacute exposures. Their data (from Figure 5 in Wehner and Craig 1972) was replotted as $\log_e$ (percent of maximum NiO deposited in lung) versus time after the end of the exposure. This plot suggests an initially rapid clearance phase (half-life ~2-5 days) followed by a much slower clearance phase between 3 and 170 days with a half-life of 84 days. In contrast, cobalt oxide (CoO) particles were rapidly cleared from the lungs of Syrian golden hamsters after exposure to CoO dust; the clearance half-life was about 1 day (Wehner and Craig 1972). Histological examination of the lungs showed accumulation of NiO particles in the lung, occasionally completely filling some of the alveoli. Particles were also noted to be phagocytized (i.e., engulfed) by alveolar macrophages.

Similarly, high lung retention and slow clearance of a nickel-enriched coal fly ash (NEFA) were reported by Wehner et al. (1979b). After 2 months of exposure to NEFA at 188 mg/m^3, 6 hours/day, 5 days/week or to fly ash (FA) at 183 mg/m^3, the hamster lungs were heavily laden with dust particles. At the end of exposure there were approximately 78 μg/lung of NEFA for a retention of about 50% (assuming 60 ml/min as the average minute volume of the hamster during exposure). The lungs of hamsters sacrificed 30 days after the end of the exposure contained a similar amount of NEFA, indicating that the dust was not readily cleared. There were no major histopathological differences among NEFA, FA, or control lungs except for the accumulation of dust in both NEFA- and FA-exposed hamsters. Chronic inhalation studies were reported to be underway.

In contrast, nickel was rapidly cleared from the lungs of mice exposed to $NiCl_2$ aerosol ($\leq$ 3 μm diameter, 644 μg Ni/m^3) for 2 hours. The clearance was exponential with a half-life of ~3 days (Graham et al. 1975).

These studies indicate the variable results on the clearance of inhaled metal salts. While a difference in aqueous solubilities between NiO and $NiCl_2$ may help explain the differences in clearances (the readily water-soluble $NiCl_2$ is rapidly cleared), other factors must contribute to the differences in CoO and NiO clearances, since both compounds are relatively insoluble, although CoO is slightly more soluble than NiO. As will be discussed later, the toxicity of inhaled particles to cilia and alveolar macrophages may help explain differences in their clearance from the lungs.

5.1.2.2 Metabolism and Excretion

The physiological effects of nickel exposure ultimately depend on the concentrations of nickel achieved at the cellular and subcellular level. The physicochemical form of the nickel determines the distribution within the body and subsequently the relative intracellular concentrations achieved.

Several studies have been done on rats of the distribution and elimination of nickel carbonyl ($Ni(CO)_4$) following an LD_{50} dosage either by the intravenous (22 mg Ni/kg) or inhalation (0.20 mg Ni/liter of air for 15 minutes) route (Sunderman and Selin 1969, Sunderman et al. 1968, Kasprzak and Sunderman 1969). The nickel carbonyl was radioactively labeled either at the carbon (^{14}C) or nickel (^{63}Ni) moiety.

An important finding of these studies was that $Ni(CO)_4$ was rapidly absorbed by the inhalation route, with levels of nickel carbonyl in the blood similar to those following intravenous administration. Gas chromatographic analysis identified $Ni(CO)_4$ as a blood species. Excretion of $Ni(CO)_4$ into expired air and elimination of $Ni(CO)_4$ from the blood were apparently monoexponential and estimates of the half-life in each case (0.6 hour for excretion and 1.6 hours for elimination) are in rough agreement, considering the imprecision of the chemical analyses. In contrast, the elimination of total nickel from the blood had a much longer half-life, 15 to 20 hours. This is interpreted to mean that nickel, once disassociated from carbonyl, is removed much more slowly from the blood. Carbon monoxide was released by the decomposition of $Ni(CO)_4$ within the body, became reversibly bound to hemoglobin, and was excreted primarily in expired air. Approximately 38% of the intravenous dose of $Ni(CO)_4$ was excreted unchanged as $Ni(CO)_4$ in the expired air, 31% was excreted in the urine,(presumably as Ni^{++}), and an almost insignificant fraction was excreted in the feces. The tissue distribution data are imprecise, but indicate a wide distribution of nickel, including to the brain and spinal column. This is interpreted to mean that $Ni(CO)_4$ is a "carrier" for nickel. The findings that $Ni(CO)_4$ was an identified species in the blood and that nickel label was found in the brain suggest that $Ni(CO)_4$ readily crosses biological membranes.

A study by Oskarson and Tjalve (1979a and 1979b) in which mice were administered approximately the same dose of $Ni(CO)_4$ (4.5 mg/Ni/kg) by either intravenous or inhalation routes also indicated that $Ni(CO)_4$ was decomposed in vivo and that most of the nickel existed in tissue in the cationic state (Ni^{++}). After inhalation, the highest levels of radioactivity (^{63}Ni) were measured in the lung, brain and spinal column, and heart muscle at 1 hour. At 1 day an extraordinarily different relative tissue distribution was seen between intravenously dosed animals and those which were dosed by inhalation. In particular, there was a much higher level in the brain in the inhalation-dosed mice. The authors suggest that the co-administration of ethanol (as vehicle) in the intravenously dosed mice may have altered the oxidation of Ni°.

In contrast to the tissue distribution of nickel carbonyl, parenteral administration of Ni^{++} leads to highest tissue levels in the kidney, endocrine glands, lung, and liver and very little in the central nervous system (NAS 1975). Organ distribution data do not ordinarily reveal the relative intracellular/extracellular distribution. A suggestion of a low intracellular penetration upon absorption or parenteral injection is made by kinetic analysis by Onkelinx et al. (1973). These researchers injected intravenously moderately small amounts of $^{63}NiCl_2$ into rats (82 µg Ni/kg) and rabbits (240 µg Ni/kg) and measured plasma concentration decline, urinary excretion, and fecal or biliary excretion. A two-compartment open system pharmacokinetic model was fitted to the data. (For discussion of the two compartment model see Greenblatt and Kock-Weser 1975.) Values of some of the important pharmacokinetic parameters normalized to a per-kilogram basis for comparison between the two species are listed in Table 5-1. Nomenclature is somewhat altered to correspond to that used in the discussion by Greenblatt and Kock-Weser.

This analysis indicates that the central compartment volume is much larger than the vascular volume (~40 ml/kg) but is close to the volume of extracellular water (~200 ml/kg). Also the peripheral compartment is quite small. The total volume of distribution ($V_1 + V_2$) is considerably less than the 600 ml/kg total body water. It should be pointed out that the computed volumes do not necessarily correspond to volumes of anatomical compartments; however, it can be tentatively concluded that nickel ion distributes primarily into extracellular water, and that it does not readily penetrate cell membranes and, therefore, would not readily cross the blood-brain barrier.

Excretion of Ni^{++} was found to be primarily via the kidney, which accounted for ~80% of excretion. Fecal or biliary excretion accounted for about 10%. Although combined urinary and fecal excretion from the central compartment was quite rapid (k of 0.1 corresponds to a half-life of 6.9 hours), the overall rate of elimination from the body was apparently reduced by the relatively slow equilibration between compartment 1 and compartment 2, such that the elimination half-life during the β phase was on the order of several days. It should be kept in mind that the values of these parameters in humans may be somewhat different (Onkelinx et al. 1973).

An extensive discussion of the binding of Ni^{++} to plasma proteins and smaller molecules (e.g., amino acids) can be found in the NAS monograph (1975). Serum albumin is the principal carrier protein. Additionally, there exist proteins with higher affinity than albumin for nickel -- so-called nickeloplasmin. The total serum nickel levels have been found to be remarkably similar among mammalian species, in the range of 1 µg/l to 8 µg/l and somewhat higher in the rabbit (U.S. EPA 1979).

Several studies indicate that serum nickel levels and urinary excretion reflect recent exposure to nickel. These studies are reviewed in the NAS monograph (1975) and the EPA criterion document (U.S. EPA 1979). These reports demonstrate that average plasma concentrations for workers in a nickel refinery were greater than for non-exposed

TABLE 5-1. PARAMETERS OF THE TWO COMPARTMENT MODEL OF ^{63}Ni(II) METABOLISM

	Rat	Rabbit
Volume of Central Compartment (ml/kg)	360	205
Volume of Peripheral Compartment (ml/kg)	40	78
Percent Excreted in Urine	78	78
Percent Excreted in Feces (bile)	15	(9)
Clearance (ml/kg/hr)	39	18
k_e, Total Elimination Rate Constant (hr^{-1})	0.108	0.088
K_u, Urinary Elimination Rate Constant (hr^{-1})	0.085	0.078
t 1/2, β Phase (hrs)	49	83

Source: Based on Onkelinx *et al.* 1973.

workers. Exposure to soluble salts of nickel or to insoluble compounds resulted in increased serum nickel levels. Spruit and Bongaarts (1977) found that serum levels of eight occupationally exposed workers averaged between 1.0 μg/dl to 1.1 μg/dl (10 μg/l to 11 μg/l) at different periods of the year, but averaged 0.53 μg/dl (5.3 μg/l) after a two week holiday. Controls showed plasma levels of 1.6 μg/l and 2.0 μg/l in males and females, respectively.

Urine nickel levels appear to be more difficult to correlate with exposure due, in part, to the difficulty of obtaining 24-hour urine specimens and avoiding inadvertent contamination. Calculation of nickel concentration relative to creatinine to control for renal function has not usually been done. Bernacki et al. (1978) analyzed both serum and urine levels of nickel in workers from 12 different occupational groups. Urine levels and serum levels generally correlated. The highest urine levels were found on average (±SD) in nickel refinery workers (124 ± 109 μg/g creatinine), nickel platers (19 ± 15), metal sprayers (16 ± 22), and nickel battery workers (10 ± 6.4). This compared with levels in non-exposed industrial workers of 2.7 ± 1.7. Individual air concentration sampling in 65 occupationally exposed workers was carried out over an eight-hour workshift. No significant correlations between the estimate of the subject's atmospheric exposure and the concentration of nickel in his urine were observed for any of the 7 occupationally exposed groups. However, the highest atmospheric levels (0.489 ± 0.560 mg/m^3) were determined for the nickel-refinery workers who also had the highest average urinary levels (124 ± 109 μg/g creatinine).

McNeely et al. (1972) conducted a study of two comparable groups of healthy hospital employees who had no occupational exposure to nickel. One population was from Hartford, Connecticut, and the other from Sudbury, Ontario. Table 5-2 presents the results of this study. On average urinary nickel excretion was higher in the Sudbury group which had higher nickel exposure from both the atmosphere and drinking water. The authors emphasize, however, that there was no evidence that the environmental exposures to nickel in Sudbury were associated with adverse effects in man or animals, or that they were deleterious in any way to the health of the inhabitants. A comparison of health effects associated with nickel exposure experienced by inhabitants from different locales would be extremely difficult to interpret because of the numerous socioeconomic and other exposure variables to be considered.

TABLE 5-2. RELATIONSHIP OF NICKEL EXPOSURE TO URINARY EXCRETION OF NICKEL

Location	Ni in Tap Water (μg/l)	Ni in Air (μg/1000 m^3)	Urinary Nickel Excretion	
			μg/1.73 m^2/day[b]	μg/g creatinine
Hartford	1.1 ± 0.3[a]	36	2.4 ± 1.3	2.3 ± 1.3
Sudbury	200 ± 43	5333	7.5 ± 3.3[c]	5.9 ± 2.8[c]

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[a] Mean ± standard deviation.

[b] Each subject's daily excretion was adjusted for his body surface area.

[c] $P < 0.001$ vs. Hartford group.

Source: McNeely *et al.* (1972)

5.1.3 Carcinogenicity

5.1.3.1 Epidemiological Studies

Nickel's role as an occupational carcinogen via inhalation, particularly in the nickel refining industry, has been given considerable study. Several recent reviews have detailed the epidemiological findings (NAS 1975, Sunderman 1973, Sunderman 1976, and IARC 1976).

A number of factors prevent any useful prediction from the epidemiological studies of the risk of respiratory tract cancer due to nickel exposure. Chiefly, there are no good estimates of the exposure to nickel of nickel workers in terms of concentrations or speciation. Concomitant exposure of workers to arsenic, chromium, cobalt, smoking, asbestos, and polycyclic aromatic hydrocarbons makes uncertain the primary role of nickel in the etiology of respiratory tract cancer. The importance of co-exposure variables has been noted in the more recent literature (see Kreyburg 1978 and Langer et al. 1980 for examples). Nevertheless, it appears to be the conclusion of most authorities who have reviewed the problem that nickel is a primary factor in the development of respiratory tract cancer in nickel refinery workers. The animal experimental data, discussed below, support this conclusion.

A careful review of all the epidemiological studies would not only be a prodigious undertaking but also seem destined to equivocation, particularly if the goal was to provide risk estimates. The inadequacy of quantative exposure data both for nickel and co-existent toxic compounds precludes evaluation of the dose-response relationship. Two studies are summarized here to illustrate a few of the problems.

Kreyberg (1978) reached no definitive conclusions concerning the relationship between nickel exposure and lung cancer, but discussed the variables of cigarette smoking, time factors, and the relative incidences of lung-tumor types among different occupational groups. Smoking was prevalent among cases of lung cancer in nickel-refinery workers; 32/39 cases were smokers. Kreyberg identified a long latency, in the range of 16 to 40 years, between first exposure to nickel and diagnosis of lung cancer. The importance of the smoking factor suggested that the latency between the start of smoking and diagnosis of cancer could be more relevant; moreover, there could be an age-dependent susceptibility to lung cancer that would partly determine the age of diagnosis. The number of cases of lung cancer roughly correlated with the number of people employed in the Falconbridge Nickel Refinery and with the availability of cigarettes. During World War II, production and the number of men employed dropped and cigarettes were a scarce commodity.

A previous study by Kreyberg had found an association between increased smoking and the incidence of lung cancer in Norway. Kreyberg stated that the true risk to a healthy person of developing lung cancer as a nickel worker could only be measured in a population of non-smokers. It is suggested, however, that a study of non-smokers may be impractical and would leave unanswered the more important question concerning interaction of smoking and nickel exposure.

Nickel carcinogenesis following ingestion does not appear to be an area for concern. This conclusion is based on the poor gastrointestinal absorption of nickel, the efficient mechanisms of excretion, and the results of animal studies which indicate that high dietary levels of nickel are without measurable carcinogenic effects.

5.1.3.2 Animal Studies

Table 5-3 summarizes the data on the carcinogenicity of nickel carbonyl. The usual route of exposure to nickel carbonyl is by inhalation. The studies of Sunderman and coworkers (1965, 1959, and 1957) suggest that nickel carbonyl is carcinogenic by the inhalation route, although there was a very poor survival rate of test animals. Kincaid et al. (1953) reported that rats who survived for 1 to 2 days after exposure to LC_{50} levels of nickel carbonyl (0.2 mg/l for 30 minutes) showed extensive pneumonitis. Those that died within several hours showed severe pulmonary congestion and edema. Histological sections showed intestial pneumonitis, areas of atelectasis, and other areas with necrosis. Large amounts of brown-black pigment were present throughout the capillaries of the alveolar walls. The acute toxicity to the lungs of nickel carbonyl has been found to be similar in experimental animals and man (see Section 5.1.4.3).

In a study by Lau et al. (1972), intravenous injection of a total of 158 mg nickel carbonyl/kg in divided doses caused a significant number of malignant tumors throughout the body over the lifetime of the rats. Intravenous injection of nickel carbonyl is comparable to inhalation because the compound rapidly distributes via the blood to all tissues when dosed by inhalation exposure. Furthermore, much of the nickel carbonyl is excreted unchanged via the lungs after either intravenous or inhalation exposure.

Survival of test rats in this study was comparable to that of untreated rats and all rats were allowed to die of "natural" causes or were killed when moribund. This study is considered adequate for risk extrapolation for nickel carbonyl.

Ottolenghi and coworkers (1974) exposed rats by inhalation to Ni_3S_2 (for details on exposure see Table 5-4), and reported highly significant lung pathology, including 14% lung neoplasms versus 1% in unexposed rats. This study is considered adequate for risk extrapolation in terms of duration, survival of test animals, number of animals tested, and the

TABLE 5-3. CARCINOGENICITY STUDIES WITH NICKEL CARBONYL ($Ni(CO)_4$)

Animal	Route/Dosage		Response [Control Data]	Reference
Wistar Rat	Inhalation:	0.03 mg/l for 30 min, 3 times per week for 12 months	1/8 rats surviving > 2 yrs had pulmonary carcinoma with metastases.	Sunderman and Donnelly (1965)
		0.6 mg/l for 30 min, single exposure	1/35 rats surviving 2 yrs had pulmonary adenocarcinoma with metastases.	
		0.6 mg/l for 30 min, single exposure treated with Dithiocarb	1/27 rats surviving 2 yrs had anaplastic lung carcinoma	
			[0/44 rats surviving at least 2 yrs had pulmonary carcinoma]	
Wistar Rat	Inhalation:	0.03 mg/l for 30 min, 3 times per week for 12 months	1/5 rats surviving > 2 yrs had neoplasms of the lung	Sunderman et al. (1957) Sunderman et al. (1959)
		0.06 mg/l as above	1/1 rat surviving > 2 yrs had neoplasms of the lung	
		0.25 mg/l for 30 min, single exposure	1/3 rat surviving > 2 yrs had neoplasms of the lung	
Sprague-Dawley Rat	Intravenous:	20 µl/kg (9 mg Ni/kg) 6 doses at intervals of 2-4 wks.	5/121 rats had pulmonary lymphomas 14/121 rats had additional malignant tumors at varied sites	Lau et al. (1972)
		50 µl/kg (22 mg Ni/kg), single dose	6/72 rats had malignant tumors at varied sites	
			[2/47 rats had pulmonary lymphomas]	
			[0/47 rats had tumors at additional sites]	

TABLE 5-4. CARCINOGENICITY STUDIES WITH NICKEL SUBSULFIDE (Ni_3S_2)

Animal	Route/Dosage	Response [Control Data]			Reference
Wistar Rat	Intratracheal: 5 mg/animal mean particle diameter 10 µm	0/13 rats had pulmonary tumors in 15 months 4/13 rats had peribronchial adenomatoid proliferation [No controls]			Kasprzak et al. (1973)
Fischer 344 Rat	Inhalation: 1 mg/m^3 6 hr/day, 5 days/week for 78 weeks Particle sizes: 70% < 1 µm 1 µm < 25% < 1.5 µm	Preneoplastic and Neoplastic Lung Lesions(%)			Ottolenghi et al. (1974
			Control	Test	
		Atypical Hyperplasia	28 (13)	106 (51)^a	
		Squamous metaplasia	10 (5)	38 (18)^a	
		Lung neoplasms	2 (1)	29 (14)^a	
		Other neoplastic findings: 12%^{a} incidence of adrenal medullary nodular hyperplasia and pheochromocytomas in test animals compared to 1% in control.			
		Other Lung Pathology(%)			
		Pneumonitis	(14)	(48)^a	
		Atelectasis	(5)	(16)^a	
		Bronchitis	(5)	(12)^a	
		Bronchiectasis	(3)	(12)^a	
		Emphysema	(6)	(11)^b	

$^a p < 0.01$

$^b p < 0.05$

thoroughness of post-mortem examination. Both males and females were tested, and there were no marked differences between the sexes in the response to the Ni_3S_2 exposure. This study is used as a basis for predicting risk of lung neoplasms in humans exposed to Ni_3S_2.

Elemental nickel and NiO have not been shown to be carcinogenic by the inhalation or intratracheal routes (Tables 5-5 and 5-6). In comparison to nickel carbonyl and nickel subsulfide, these nickel compounds caused less severe adverse pulmonary reactions. Further discussion of pulmonary toxicity appears in Section 5.1.3.1.

5.1.3.3 Carcinogenicity Studies Using Other Routes of Administration

As has already been discussed, nickel salts are poorly absorbed via the oral route. There has been no demonstration of carcinogenic activity by the oral route in humans or in animals (NAS 1975, U.S. EPA 1979).

Numerous investigators have administered intramuscular, subcutaneous, or intraperitoneal injections of nickel and nickel compounds to induce local sarcomas as a preliminary step in studying morphology, biochemistry, and the effects of chemotherapeutic regimens in cancer. Sunderman (1976) remarked that Ni_3S_2 carcinogenesis is an attractive experimental model because the compound is inexpensively available in high purity and is readily labeled with ^{63}Ni, which is ideally suited for liquid scintillation spectrometry and auto-radiography.

However, injection-site tumors from nickel compounds are probably not relevant to the risk assessment. On the one hand, the IARC working group (IARC 1976) has pointed out that injection-site tumors require careful consideration because of the possibility of non-specific action of the vehicle or the physical effect of the agent. Injections of finely divided forms of nickel compounds are not comparable to the exposure of human populations. It has been noted that carcinogenicity following subcutaneous injections is inversely related to solubility of the injected nickel compound. Clearly, one of the reasons for this is that soluble salts do not remain at the injection site, but are carried away and rapidly excreted.

On the other hand, the insoluble nickel compounds have been demonstrated to be slightly soluble in *in vivo* and *in vitro* experiments. Nickel ion is complexed with many large (proteins) and small (e.g., amino acids) molecules so that transport across cellular membranes (by phagocytosis, pinocytosis, facilitated transport) does occur. Intracellular Ni ion affects metabolism and in particular becomes closely associated with nuclear elements (Sunderman 1976). Nickel is one of the metals in the stainless steel alloys used in implant materials such as for bone fixation, joint replacement, and heart valves. The reports of two cases of tumors in humans at the sites of stainless steel implants (NAS 1975) and allergic sensitivity reactions to stainless steel implants that resolved after the implants were removed (U.S.

TABLE 5-5. CARCINOGENICITY STUDIES WITH ELEMENTAL NICKEL

Animal	Route/Dosage	Response [Control Data]	Reference
Mouse	Inhalation: 15 mg/m^3, 6 hr/day, 4-5 days/week until death, 99% pure - particle diameter < 4 μm	No abnormalities of bronchial mucosa	Hueper (1958)
Rat Guinea Pig	Same	15/50 rats and most guinea pigs showed abnormal multicentric adenomatoid formation affecting alveolar structures and atypical proliferations of the epithelial lining of the terminal bronchioli . Rats showed inflammatory changes and mucosal ulcers in the para nasal sinuses. 1 group showed anaplastic intraalveolar carcinoma, extensive adenomatosis, and a possible metastasis from lung in the abdominal cavity. [Control: the adenomatosis seen in the test group of guinea pigs was noted in 5/9 controls but was not diffuse as in test animals. Generally, there are inadequate control data].	
Rat Hamster	Inhalation: level unspecified 99% pure - plus 20-35 mg/kg (sic) SO_2 and powdered limestone 1 part to 3-4 parts Ni (to prevent conglomerates)	0/46 tumors in rats surviving > 18 months 0/66 tumors in hamsters surviving > 18 months	Hueper and Payne (1962)

TABLE 5-6. CARCINOGENICITY STUDIES WITH NICKEL OXIDE (NiO)

Animal	Route/Dosage	Response	Reference
Hamster	4 mg/animal once a week for 30 weeks by intratracheal injection. Particle diameter: 0.5-1.0 μm	1/50 tumor of respiratory tract in test animals.	Tarrell and Davis (1974)
	Controls received nut-shell charcoal in place of NiO	4/50 tumors of respiratory tract.	
Syrian Golden Hamster	Inhalation: 52 μg/l, 7 hrs/day 5 days/week for lifespan. Particle diameter: 0.3 μm	4/51 malignant tumors at various sites. 1/51 controls. Authors concluded no carcinogenic effect due to NiO.	Wehner et al. (1975a) (1975b) (1979a)
	Asbestos fiber inhalation 23 μg/l	10/102 lung adenomas	

EPA 1979) suggest that the alloys are not totally inert. The cases of tumors at implant sites in humans are anecdotal. Comparisons of these complications and those with other implant materials and appropriately controlled studies would have to be carried out to assess whether or not tumorigenesis associated with internal protheses is a significant health problem.

The injection-site tumorigenesis of nickel in experimental animals has been extensively reviewed elsewhere (NAS 1975, U.S. EPA 1979, Sunderman 1973, and Sunderman 1976).

5.1.3.4 Mechanisms of Nickel Carcinogens

Various lines of research have been pursued to determine the mechanisms of nickel carcinogenesis. An essential first step is penetration of the cell membranes by the nickel compounds. As discussed above, nickel carbonyl can diffuse across biological membranes because of its lipid solubility and relative stability *in vivo*. It decomposes, liberating Ni° which is then oxidized to Ni^{++}. Ni^{++} has been shown to react with a variety of intracellular constituents. Nickelocene is also lipophilic and, therefore, would be expected to penetrate biological membranes by diffusion.

Singh and Gilman (1973), using a double-diffusion chamber implanted intraperitoneally in rats, demonstrated that nickel subsulfide had a sufficient solubility *in vivo* to diffuse across a filter of pore size 0.1 μm and to disrupt the normal growth of embryonic rat skeletal muscle in the adjacent chamber.

Webb and coworkers have shown that metallic nickel powder gradually dissolved when incubated with horse serum or muscle homogenates and that the nickel is complexed with serum proteins and ultrafilterable molecules (Heath *et al.* 1969, Weinzierl and Webb 1972). Webb and Weinzierl (1972), using cultured C57S/1P mouse dermal fibroblasts, studied the cellular uptake from media containing $^{63}Ni^{++}$ complexes and the relative intracellular distribution of ^{63}Ni. The concentration in the culture media was 7-10 μg/ml of Ni^{++} complexes. After 48 hours, approximately 3.5% of ^{63}Ni was bound to the cell monolayer and 97% of this was released when trypsinization of the monolayer was performed to separate cells and isolate them. The nickel content in the isolated cells was 0.023 μg ^{63}Ni or 0.04% of the nickel available from the media. The approximate intracellular distribution determined after fractionation was nuclear fraction, 37%; cell sap fraction, 30%; mitochondrial fraction, 23%; and microsomal fraction, 11%. Of the nuclear fraction, 50% was isolated with the nucleoli and 20% with the nuclear sap. The authors do point out, however, that the quantitative measurements of intracellular distribution are subject to certain limitation because losses and transfers between fractions may occur during cell isolation and the fractionation procedure. While intracellular uptake of Ni^{++} is indicated, it is clearly extremely low.

Phagocytosis of insoluble nickel compounds by alveolar macrophages (Johansson and Camner 1980) and by Syrian hamster embryo cells and Chinese hamster ovary cells (Costa and Mollenhauer 1980) demonstrates another means of intracellular transport. Once within the cell enclosed in vacuoles, the particles are subjected to catalytic enzymes and altered pH which could ultimately release nickel intracellularly. Johansson and Camner (1980) proposed that alveolar macrophages may transport nickel to lymph nodes. These researchers exposed rabbits for 3 months (5 days/week, 6 hours/day) to metallic nickel dust (1.2 mg/m^3) and reported finding nickel particles within macrophages from the hilar lymph nodes. They concluded that the macrophages containing nickel particles passed across the alveolar wall and then to the nodes. They also concluded that the nickel particles did not cross the alveolar walls to be subsequently taken up by macrophages because of morphological similarities of the "laminated bodies" found in both the alveolar and lymph node macrophages.

Sunderman and coworkers have studied the intracellular mechanisms of Ni toxicity. In the initial study (1967a) on this aspect of Ni toxicity, Sunderman found that $Ni(CO)_4$ administered to rats at LD_{50} dosage by either intravenous injection (22 mg Ni/kg) or inhalation (0.2 mg Ni/1 air for 15 minutes) inhibited phenothiazine induction of hepatic cell benzpyrene hydroxylase activity. Maximum inhibition occurred when $Ni(CO)_4$ was administered approximately 24 hours before induction. In vitro benzpyrene hydroxylase activity was not inhibited by added Ni^{++}. That benzpyrene hydroxylase synthesis was probably inhibited was indicated in a second study (1967b). Nickel carbonyl (LD_{50} dose, IV) inhibited cortisone induction of hepatic tryptophan pyrrolase activity; however, the enzyme activity was not significantly different between control and test [$Ni(CO)_4$ pretreatment of rats] preparations when tryptophan was administered to increase the enzyme levels. Tryptophan increases hepatic tryptophan pyrrolase activity by decreasing the enzyme's catalysis, while cortisone increases synthesis of messenger RNA template for enzyme production.

Further evidence that Ni inhibited synthesis of heptatic enzymes was reported by Sunderman in 1968. In this experiment the effect of nickel carbonyl (LD_{50} dose) on induction of hepatic cytochrome P-450 activity was studied. The enzyme was measured spectrophotometrically so that changes in levels of important co-factors in enzyme reactions could be discounted as a cause of the ability of Ni^{++} to block induction of hepatic enzyme activity. $Ni(CO)_4$ inhibited the induction of the enzyme, not the enzyme's in vitro activity. In this case, there was a definite reduction in tissue concentration of the cytochrome P-450 from $Ni(CO)_4$-treated rats compared to the concentration in control tissue.

Beach and Sundeman (1970) further clarified the site of action of nickel carbonyl by demonstrating that administration of the compound to rats inhibited RNA synthesis by the chromatin-RNA polymerase complex prepared from lysed hepatic nuclei. Thus, inhibition due to impaired transport of RNA precursors across the nuclear membrane was apparently ruled out. Control chromatin-RNA polymerase complex was not inhibited when treated in vitro with $Ni(CO)_4$ or $Ni\ Cl_2$ at concentrations 3 times higher than the Ni concentration remaining in the in vivo treatment preparation. This result suggested that Ni^{++} does not interfere with RNA synthesis directly but at some earlier step, perhaps at the DNA level.

The effects demonstrated by Sunderman and coworkers do not necessarily represent carcinogenic mechanisms but may be relatively nonspecific toxic responses of physiologically damaged cells. The high toxic dose of nickel carbonyl should be expected to have a multitude of effects at the biochemical level, many of them indirect and nonspecific. The penetration to and disruption of nuclear processes by nickel may be secondary to cellular damage because the cell cannot maintain the normal membrane barriers and intracellular milieu. An inference that these studies may illustrate a co-carcinogenic role of nickel (as nickel carbonyl) is also probably unwarranted because the doses were extremely high.

5.1.3.5 In Vitro Assays of Carcinogens

DiPaolo and Casto (1979) studied inorganic metal salts in a transformation assay using Syrian hamster embryo cells (HEC). Salts of nickel, cadmium, chromium, beryllium, and arsenic were positive (induced transformation of cells) in this assay, but salts of iron, titanium, tungstate, zinc, aluminum, and amorphous nickel sulfide (NiS) were negative. With the exception of the results for cadmium, these results generally correlate with those from animal and/or human studies of carcinogenicity. In a later study (Costa et al. 1979), undifferentiated sarcomas developed in 26 of 27 nude mice at the site of subcutaneous injection of clones of Ni_2S_3-transformed cells, and no tumors developed in 19 control nude mice given subcutaneous injections of control, non-transformed Syrian hamster embryo cells. Costa and Mollenhauer (1980) determined that amorphous NiS was not phagocytized by Syrian hamster embryo cells or by Chinese hamster ovary cells but Ni_3S_2 was actively phagocytized. These authors suggest that carcinogenicity may be dependent on cellular uptake.

Nishimura and Umeda (1979) and Umeda and Nishimura (1979) studied the ability of metal compounds to induce chromosome aberrations in FM3A cells from C3H mouse mammary carcinoma. Compared with chromium (+6 valency) compounds, Ni compounds were poor inducers of chromosome aberrations. Aberrations, principally gaps, were greater than in control cultures at concentrations between 2 and 10 x 10^{-4}M. Twenty x 10^{-4}M was lethal to the cultures. The ability of Ni compounds to induce chromosome aberrations became somewhat more apparent when cells were first treated in various Ni media (6 to 10 x 10^{-4}M) for 24 or 48 hours and then incubated in control medium. During recovery, the percentage of aberrant chromosomes, again principally gaps, tended to reach a maximum after 24 or 48 hours and fall off to control levels after 1 or more days. Taking the overall incidence presented by Nishimura and Umeda, the nickel compounds appear to induce low levels of chromosomal aberrations at concentrations that are also toxic to the cells. It should be noted that the aberrations induced are mostly, if not exclusively, gaps which are not scored as chromosomal aberrations by some investigators because of the subjective nature of scoring gaps.

5.1.4 Other Toxicological Effects

5.1.4.1 Chronic Inhalation Toxicity

Low-level chronic inhalation toxicity to nickel compounds has not been studied in man or animals adequately to make estimates of levels of exposure which cause no effects. A brief report by Torjussen and Solberg (1976) on a pilot study stated that of 92 nickel-exposed workers, 17% were found to have had atypical epithelial changes in nasal biopsy specimens from the mucosa of the middle turbinate. No such changes were found in the 37 controls who had no known exposure to nickel. Exposure levels and a description of the study population were not given in this report. Both carcinogenic response and non-carcinogenic lung pathology have been summarized in Tables 5-3 through 5-6. The results for Ni_3S_2 inhalation in rats (Ottolenghi and coworkers 1974) are particularly alarming.

Wehner and coworkers (Wehner and Craig 1972, Wehner *et al.* 1975a, Wehner *et al.* 1975b, Wehner *et al.* 1979a, Wehner *et al.* 1979b) have studied the inhalation toxicity of NiO, CoO, and chrysotile asbestos. Differences in the clearance of NiO and CoO from the lungs were found. Histopathological evaluation of lung sections from chronically exposed hamsters (53 mg NiO/m^3, 7 hours/day, 5 days/week) indicated accumulation of NiO within the alveoli. After short periods of exposure (unspecified by the authors but presumed to be on the order of months), there was little cellular response. After longer periods of exposure, the nature of the cellular response was both inflammatory (macrophage accumulation containing phagocytized NiO particles) and proliferative ("alveolar septal cell hyper-plasia," "epithelial proliferations from bronchioles, and bronchiolization of alveoli"). Pneumoconiosis was more pronounced in the NiO-exposed animals than the CoO-exposed animals. Pneumoconiosis was defined to "include interstitial pneumonitis and diffuse granulomatous pneumonia which were frequently more severe in focal areas, fibrosis of alveolar septa, bronchial and bronchiolar (basal cell) hyperplasia, bronchiolization of alveolar epithelium, squamous metaplasia, and emphysema and/or atelectasis of varying degree." There was no clearer breakdown relating duration of exposure to incidence of specific respiratory tract lesions.

Wehner and coworkers found no malignant tumors or premalignant lesions of the respiratory tract in hamsters exposed to NiO for their entire lifetime (53 mg/1, 7 hours/day, 5 days/week). In 102 asbestos-exposed hamsters, 10 lung adenomas were seen. These lesions are considered to be premalignant. Two other lung adenomas were apparently seen but in which groups they occurred could not be determined from the investigators' reporting.

Since alveolar macrophages are considered an important defense mechanism against inhaled substances such as bacteria, reports of the toxicity of respirable metal dusts to alveolar macrophages are of some interest. It is unclear, however, what indexes of toxicity are appropriate and what levels of toxic response can be considered as deleterious to humans.

Graham and coworkers (1975) measured the viability and phagocytic activity of alveolar macrophage (obtained from untreated rabbits). The alveolar macrophages were treated _in vitro_ with VO_3, Ni^{++}, Cd^{++}, Cr^{+++}, and Mn^{++}. Ni^{++} markedly decreased phagocytic activity of alveolar macrophages at concentrations (e.g., 0.8 mM) that were only slightly cytotoxic, while VO_3^- was cytotoxic at concentrations (e.g., 0.7mM) that did not affect phagocytic activity of the remaining viable macrophages. With Cd^{2+}, Cr^{3+}, and Mm^{2+}, viability and phagocytic activity were decreased more in parallel.

In contrast to Graham's results, Camner _et_ _al._ (1978) measured an apparent increased phagocytic activity (uptake of silver-coated Teflon particles _in vitro_) of alveolar macrophages obtained from rabbits exposed to metallic Ni dust (0.5 or 2.0 mg/m^3 for 4 weeks, 6 hours/day, 5 days/week) when compared with macrophages from non-exposed rabbits.

Aranyi _et_ _al_. (1979) studied the effects of coal fly ash (FA) coated with PbO, NiO, or MnO_2 on alveolar macrophages obtained from untreated rabbits. The order of toxicity based on viability, total protein content, or lactic dehydrogenase activity was PbO/FA > NiO/FA > MnO_2/FA > untreated FA. Decreased viability appeared to be the most sensitive indication of toxicity.

Another defense mechanism of the lung is muco-ciliary clearance. Adalis and coworkers (1978) reported that Ni at concentrations of 0.011 mM decreased ciliary beating frequency in an _in vitro_ model using isolated hamster tracheal rings. Exposure of hamsters to $NiCl_2$ aerosol at concentrations of 100 to 275 µg of nickel/m^3 (2 hours/day for 1 or 2 days) also decreased ciliary beating frequency as determined _in vitro_. The tracheal rings were removed from the treated animals 0, 1, 2, or 3 days after the exposure for the _in vitro_ tests. The beating frequency was depressed at all times compared to control.

One of the possible consequences of these effects was indicated in studies by Port and coworkers (1975) and Adkins and coworkers (1979). Port reported that NiO (intratracheal instillation of 1-5 mg, <5 µm diameter) significantly increased mortality from an influenza virus in hamsters. Mortality was highest when NiO was administered 24 hours before the influenza virus exposure (route not indicated). Pathological changes in the lung were exacerbated when the sequence of influenza NiO exposure was reversed. Adkins reported increased mortality due to inhaled streptococci in mice pretreated with a 2-hour exposure to nickel chloride aerosol (499 ug Ni/m^3). He also reported a significant reduction in phagocytic activity of alveolar macrophages obtained 24 hours after nickel chloride exposure.

5.1.4.2 Reproductive Effects

The embryotoxicity and teratogenicity of nickel carbonyl were reported in abstract form by Sunderman and coworkers (1978a). Pregnant rats were exposed on day 8 of gestation to $Ni(CO)_4$ by inhalation in dosages of 0.06 mg/l or 0.12 mg/l air for 15 minutes. These two dosages correspond to approximately 1/10th and 1/5th the LD_{50} dosage. Table 5-7 indicates significant embryotoxic and teratogenic effects of nickel carbonyl.

In another study, Sunderman and coworkers (1978b) found no teratogenic effects of either nickel chloride (16 mg/kg) or nickel subsulfide (80 mg/kg) in rats. Dams were injected intramuscularly on Day 6 or 8 of gestation. Results showed that nickel ion did cross the feto-maternal barrier. The effects that were seen were a reduced number of pups per dam and diminished body weights of the fetuses and weanlings 4 to 8 weeks after birth.

Feeding studies have tended to show adverse effects of nickel salts on reproduction. Schroeder and Mitchener (1971) followed three generations of rats continuously exposed to nickel (as Ni^{++}) in drinking water at 5 mg/l. This level corresponds to approximately 0.4 mg/kg/day (5 mg/l x 0.025 liters/day ÷ 0.3 kg b.w.). Increased numbers of runts and increased neonatal mortality were seen in each generation. Moreover, there were significant reductions in litter size and a reduced male/female sex ratio in the third generation.

Ambrose and coworkers (1976) followed three generations of rats given nickel in their diet at 250-1000 mg/kg. Assuming food consumption is normal at ∿ 15 gm/rat, these levels correspond to ∿ 4 and 15 μg/rat or 1750 to 7000 times average human nickel intake. Food consumption was reduced at the 1000-mg/kg level in all generations and, perhaps for this reason as well as nickel toxicity, there was increased fetal mortality in the first generation.

Subcutaneous dosing of 2.4 mg Ni/kg to male rats caused abnormal histopathology of the testis with disintegration of spermatozoa 18 hours after a single dose; the effects were reversible (Hoey 1966). Another study cited by NAS (1975) also demonstrated gametotoxic effects in rats dosed orally with 25 mg/kg. The male rats were apparently infertile. Gametotoxic effects have not been documented in humans.

TABLE 5-7. EMBRYOTOXIC AND TERATOGENIC EFFECTS OF INHALED NICKEL CARBONYL

	Response to Treatment (±SD)		
Dosage, mg/1 x 15 min	0	0.06	0.12
Live Fetuses/Dam	9.2 (± 2.1)	7.2 (± 3.1)	6.3 (± 4.7)[a]
Dead Fetuses/Conceptuses	4/114	2/45	15/59[a]
Body Weight of Live Fetuses	3.4 (± 0.2)g	3.0 (± 0.4)g	2.8 (± 0.3)g
Ophthalmic Malformations	0/110	12/43[a]	12/44[a]

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[a] $P < .02$

Source: Sunderman *et al.* (1978a)

5.1.4.3 Acute Toxicity of Nickel Carbonyl

Nickel carbonyl is probably the most toxic nickel compound. Because of this and because of its likely carcinogenic and teratogenic effects, it requires special consideration. The acute toxicity is similar in animals and humans; nickel carbonyl is about 100 times as toxic as carbon monoxide. Table 5-8 shows that central nervous system effects predominate initially upon acute exposure.

As has been indicated in animal studies, there is rapid distribution of nickel carbonyl to all tissues, roughly in proportion to blood supply, and ready passage across cell membranes. Excretion via lungs is an important means of elimination. Intracellularly nickel carbonyl breaks down to Ni° and CO. CO is subsequently handled as in carbon monoxide poisoning; it binds hemoglobin competitively displacing oxygen carrying capacity and is slowly excreted primarily as CO in exhaled gases. Ni° is oxidized to Ni(II) and much of it becomes bound to serum proteins. Serum Ni(II) is rapidly cleared via the kidney.

Due to the rapid and extensive distribution in the body of nickel carbonyl, most tissues are affected but the lung is the primary target organ. Kincaid and coworkers (1953) reported that after a 30-minute inhalation exposure in rats to 0.24 mg/l, pulmonary congestion and edema were apparent at one hour. Twelve hours to 6 days later lung histopathology was reported as interstitial pneumonitis with focal atelectasis and necrosis. Focal necrosis was apparent in other major organs. The pathologic lesions of the lung in human exposure are very similar (NAS 1975).

Recovery from nickel carbonyl poisoning is slow, requiring several weeks. Prompt administration of chelating agents, most notably sodium diethyldithiocarbamate, significantly reduces the severity of toxicity and is indeed life-saving.

5.1.4.4 Nickel Dermatitis

Nickel allergy has been recognized as an occupational problem where workers are exposed to nickel and its salts, particularly in nickel mining and refining. Other sources of occupational exposure include manufacture or use of nickel-cadmium batteries, nickel catalysts, ceramics, duplicating machines, certain dyes and inks, electronics, electroplating, jewelry making, rubber, and spark plug manufacturing (NAS 1975). According to the NAS report, occupational exposure is less of a problem today than in the past due to improvements in protecting workers from exposure, but non-occupational exposure, principally through skin contact, is very widespread. Sources include jewelry, coinage, clothing fasteners, tools, cooking utensils, stainless steel kitchens, detergents, prostheses and other medical appliances, and tobacco smoke.

The seriousness of the problem in the non-occupational setting is difficult to evaluate in terms of pain and suffering, but probably is

TABLE 5-8

CLINICAL MANIFESTATIONS OF NICKEL CARBONYL POISONING IN 25 MEN[a]

Immediate symptoms	Dyspnea (80%), fatigue (80%), nausea (76%), vertigo (44%), headache (36%), odor of "soot" in exhaled breath (36%), vomiting (24%), and insomnia and irritability (24%)
Latent period	In half of the subjects, an asymptomatic interval between recovery from initial symptoms and onset of delayed symptoms
Delayed symptoms	Dyspnea with painful inspiration (80%), nonproductive cough (64%), muscular weakness (44%), substernal pain (44%), chilling sensations (32%), muscular pain (28%, sweating (24%), visual disturbances (12%), diarrhea (12%), abdominal pain (4%), muscle cramps (4%), and hypoesthesia in legs (4%)
Physical and x-ray findings	Tachypnea and tachycardia (80%), interstitial pneumonitis on x-rays (60%), fever (40%), and cyanosis (36%)
Laboratory findings	Pulmonary-function tests consistent with interstitial lung disease (40%), increased serum glutamic pyruvic transaminase (36%), increased serum glutamic oxaloacetic transaminase (32%), and low arterial pO_2 (32%)
Clinical course	Interval before hospitalization: median, 2 days; range, 0-7 days. Duration of hospitalization: median, 6 days; range, 0-27 days. Interval before recovery: median, 38 days; range, 1-88 days. Symptoms that persisted for more than 3 weeks: fatigue (88%), exertional dyspnea (52%), muscular weakness (48%), headache (36%), abdominal pain (36%), muscular pain (32%), sweating (24%), visual disturbances (16%), and muscle cramps (8%).

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[a] Based on observations of Vuopala _et_ _al_. (1970)

Source: NAS (1975)

not directly life-threatening. The incidence of nickel allergic contact sensitivity has been variously estimated between about 5 and 12% and is much more common in women than in men. Fisher (1967) found that nickel caused more instances of dermatitis than all other metals combined.

The chemical pattern of nickel dermatitis begins as itching or burning (papular erythema); this usually occurs at the sites of contact (suspenders, earrings), but often can become far removed from the apparent area of contact. The eruption usually presents as a papular (raised bumps) or papulovesicular (bumps with blisters) dermatitis with a tendency for lichenification (thickening of the epidermis). A puzzling feature of nickel dermatitis is that some cases persist for months after removal of the apparent offending agent; nickel fixation in the skin and subtle re-exposure to environmental nickel products have been hypothetized as reasons for the chronicity (NAS 1975).

5.1.5 Summary

5.1.5.1 Derivation of the Water Quality Criteria

The water quality criteria for nickel were based on the results of the study by Schroeder and Mitchener (1971) which indicated toxicity to rats in a three-generation reproduction study (increased neonatal mortality, increased numbers of runts, and reduced male/female sex ratio). Test animals were given nickel in the drinking water at 5 mg/l which, with nickel in food included, was calculated by the EPA (U.S. EPA 1980) to be approximately 0.443 mg/kg/day. Using an uncertainty factor of 1000, the average daily intake (ADI) was computed for a 70-kg human as 0.031 mg Ni/day. A water concentration of 13.4 mg/l was calculated that would give this ADI assuming 2 liters of water/day plus 0.0065 kg/day of fish/shellfish products with a bioconcentration factor 47 for nickel.

The EPA (U.S. EPA 1980) states that the average drinking water levels are 6 μg/l; however, nickel in water contributes only about 2-3% of total nickel ingested because food is the major source of ingestion of nickel.

5.1.5.2 Additional Health Effects in Risk Assessment

Exposure to nickel salts through ingestion would appear to pose very little risk because of very low gastrointestinal absorption and the presence of efficient excretion mechanisms for elimination of nickel from the body.

The principle routes of exposure to nickel compounds which are associated with adverse effects are inhalation and skin contact. Nickel workers who are exposed to a variety of nickel compounds are one of the special groups at risk. Animal studies indicated that nickel carbonyl or respirable particulates containing nickel subsulfide were carcinogenic and that other insoluble nickel compounds caused adverse effects on the lungs. These data tend to support the view that certain nickel compounds were causally related to the increase in respiratory tract cancers in nickel workers. The ability of various insoluble nickel compounds to cause pneumonitis and atypical cellular changes in the upper respiratory tract may suggest a co-carcinogenic role of these nickel compounds or at least some synergy in the development of lung diseases.

Nickel carbonyl is an extremely poisonous substance and is probably carcinogenic.

The other major effect of nickel is dermatitis which has been an occupational problem in industries where exposure to nickel compounds is common. The most frequent non-occupational causes of nickel dermatitis are contact with clothing fasteners and jewelry (e.g., rivets, snaps, earrings, costume jewelry). The actual incidence is not known, but some sources suggest nickel is the major offender in contact sensitivity to metals.

5.1.6 Carcinogenic Dose-Response Relationships for Two Nickel Compounds

5.1.6.1 Introduction

In this section the potential carcinogenic risk to humans due to inhalation of either nickel carbonyl or nickel subsulfide is estimated. Note that the carcinogenic dose-response relationships obtained here may not be applied to pure nickel or any other nickel compounds and are limited to inhalation exposure. Dose-response relationships were determined for these two nickel compounds because the nickel in ambient air, in the occupational environment, and in cigarette smoke may be in the form of either or both of these nickel compounds.

Ideally, the carcinogenic dose-response extrapolation would be approached from two directions:

- Given human dose-response data (generally taken from retrospective studies of past occupational exposure or of unusually high ambient exposure levels), various extrapolation models would be applied to obtain an approximate dose-response relationship (a relationship giving percent excess carcinogenic response as a function of daily dose or exposure level).

- Given dose-response data for controlled experiments on laboratory animals, the animal doses would be converted to estimated equivalent human doses and, again, the various extrapolation models would be applied to obtain an approximate human dose-response relationship.

The advantage of the first approach is that the results are of obvious relevance to humans, since the "test" subjects are human. However, in retrospective studies of human exposure, the exposure levels, duration of exposure, and even response rates are usually only best estimates. Unknown factors (background effects, exposure to carcinogens other than the one in question, etc.) may seriously bias the data.

The advantage of the second approach is that the exposure, response, and general living conditions of the laboratory animals are known since they are design parameters or experimental variables. Also, controlled experiments can yield a broader range of precise dose-response data points, which allows straightforward application of the extrapolation models, sometimes not possible based on the sparse data from human retrospective studies. However, species differences in susceptibility, pharmacokinetics, repair mechanisms, and the calculation of equivalent human dose based on animal dose add considerable uncertainty to a quantitative risk assessment.

Beyond the uncertainties associated with this type of data, there are other important and largely unquantifiable sources of uncertainty in this analysis.

- The main purpose of risk analysis is to extrapolate from response rates observed at high exposure levels to response rates (risks) at the relatively low exposure levels that might be found in the environment. The validity of the extrapolation models, however, cannot be tested at low exposure levels (low enough to keep excess lifetime risk per capita around 10^{-5}). Inadequate understanding of the mechanisms of carcinogenesis presents no basis for choice among a variety of different mathematical models. These models make similar risk predictions at high exposure levels, but markedly different predictions at low exposure levels. No attempt is made here to quantify the uncertainty inherent in the choice of an extrapolation model; rather, a variety of models are applied to establish a range of potential risk. Also, no attempt is made to determine statistical confidence bounds. It is felt that the quantifiable uncertainties inherent in this analysis would make such a statistical exercise meaningless.

- Whether the test subjects are humans or laboratory animals, in most cases they only very rarely have been exposed to the carcinogen in question for an entire lifetime. To estimate potential risk due to lifetime exposure when the exposure period is significantly less than the lifetime of the test subjects, a simple linear conversion is performed to determine a lifetime daily dose equivalent in mass to the actual dosage. However, this extrapolation of intermittent or short-duration exposure to equivalent daily lifetime exposure largely disregards such factors as latency of effect, recovery by normal repair mechanisms (i.e., existence of a true threshold level), age-specific susceptibility (possibly due to correlated age-specific exposure to other toxicants), and acute toxicity at high levels that may alter cellular defenses against a carcinogenic effect. The conversion of short-term exposure to lifetime equivalent exposure may represent one of the most significant short-comings of the risk extrapolation.

- Peculiarities, such as the lack of control groups or contradictory results from equally valid studies, may make analysis difficult. After the elimination of irrelevant or highly questionable studies, this analysis was based on the study whose results showed the greatest adverse effects; thus, the analysis is conservative

In summary, the potential lifetime carcinogenic risk to humans of a substance can be estimated by applying a variety of dose-response extrapolation models to human dose-response data and/or to human equivalent dose-response data based on laboratory animal data. Uncertainty arises in the estimation of human exposure and response in the conversion of animal exposure to human equivalent exposure, and in the application of the dose-response extrapolation model themselves. Even greater uncertainty arises in the conversion of short-term exposure to equivalent lifetime exposure.

Nevertheless, in the absence of any other more acceptable methodologies, these procedures are currently endorsed by the EPA (U.S. EPA 1980a). While these procedures do permit a rough quantitative approximation of risk, the predictions must be interpreted with considerable caution.

5.1.6.2 Dose-Response Models for Estimation of Human Risk

The three dose-response models used to extrapolate human risk are the linear "one-hit" model, the log-probit model, and the multi-state model. The latter is actually a generalization of the one-hit model, in which the hazard rate is taken to be a quadratic rather than linear function of dose. All of these models are well known in the literature, and a theoretical discussion may be found in Arthur D. Little, Inc. (1980).

The one-hit and multi-stage models assume that the probability P(x) of carcinogenic response to average daily lifetime dose x is described by

$$P(x) = 1 - e^{-h(x)},$$

where h(x) is the "hazard rate" function. The log-probit model assumes that human response varies with dose according to a log-normal distribution. Due to their differing assumptions, these models usually give widely differing results when effects data are extrapolated from relatively high doses to the low doses typical of environmental exposure.

For the linear one-hit model, the hazard rate function is $h(x)=Bx + C$, where the parameters B and C indicate carcinogenic response attributable to dose x and background carcinogenic response, respectively. Solving for B from the data, then the probability of carcinogenic response attributable to dose x is given by

$$P(x) = 1 - e^{-Bx}.$$

For the log-probit extrapolation, the equation

$$P(x) = \Phi\left(A + \log_{10}[x]\right)$$

is solved for the "probit" intercept A, where Φ is the cumulative normal distribution function, and P(x) is the excess probability of response of exposed groups over unexposed groups. This equation makes the assumption that the log-probit dose-response curve has unit slope with respect to the log-dose. Tables of the standard normal distribution are used to find A, and then this value is used to determine the probability of a response at various exposure levels.

The multi-stage model with a quadratic hazard rate function,

$$h(x) = ax^2 + bx + c,$$

is fit to the data, if enough are available. To estimate the parameters a, b, and c, a maximum-likelihood method is used, aided by a computer program which performs a heuristic search for the best fit. The parameter b dominates for small values of dose x, and parameter a dominates for large values. The probability of response attributable to dose x is then

$$P(x) = 1 - e^{-(ax^2 + bx)}.$$

5.1.6.3 Nickel Carbonyl

For nickel carbonyl, the best carcinogenicity data (amenable to dose-response extrapolation) currently available are from a study on Sprague-Dawley rats administered nickel carbonyl intravenously (Lau et al. 1972). The data selected for analysis are listed in Table 5-9. The data used are the incidences of malignant tumors at all sites in treated and control rats.

The assumption for determining the human dose equivalent to an animal dose is that recommended by the EPA (U.S. EPA 1980a), which normalizes the dose rate according to body surface area. This approach is relatively conservative, in that it results in a lower equivalent human dose than would be obtained from adjusting dose on a per-kilogram body-weight basis. Whether surface area or body weight is the more appropriate normalization factor is open to debate.

The equivalent lifetime dose D for the rat is simply the total dose divided by the average lifetime of the rat (which was approximately 2 years in the study):

TABLE 5-9. CARCINOGENIC RESPONSE IN SPRAGUE-DAWLEY RATS TREATED INTRAVENOUSLY WITH NICKEL CARBONYL

Rat Dose	Equivalent Human Ingestion Dose (mg/day)	Response	Percentage(%)	Percentage Excess Over Controls(%)
20 μl/kg, 6 doses at 2-4 week intervals	2.5	19/121	16	12
0μl/kg	0	2/47	4	-

Source: Based on data from Lau *et al*. (1972)

$$D = \frac{20\ \mu l/kg/dose \times 6\ doses \times 1.318\ mg/\mu l}{2\ yr \times 365\ days}$$

$$= 0.217\ mg/kg/day$$

From EPA guidelines (U.S. EPA 1980a), the linear one-hit parameter B for test animals, B_A, is given by

$$B_A = \ln \left[\frac{1 - P_C}{1 - P_T}\right] \div D = 0.587 \text{ per (mg/kg/day)},$$

where P_C and P_T are the control and test group response ratios, respectively. To determine the parameter B_H for humans, surface area adjustments are made as follows:

$$B_H = B_A \left(\frac{70\ kg}{.3\ kg}\right)^{1/3} \qquad = 3.6 \text{ per (mg/kg/day)}$$

$$= 0.05 \text{ per (mg/day)},$$

where 70 kg and .3 kg are the average masses of humans and rats, respectively.

In order to estimate risk due to inhalation exposure, one must know the respiratory retention of nickel carbonyl and assume an equivalence of effect from the absorbed does by either intravenous or inhalation routes. In the absence of the retention factor, one should interpret the value B_H only in terms of dose absorbed into the blood. It cannot be assumed that ingested nickel carbonyl is equivalent to intravenous or inhalation absorption, since the effect of gastric contents on nickel carbonyl degradation is not known. In any event, ingestion exposure to nickel carbonyl is rare and probably does not occur normally because of the instability of nickel carbonyl in the environment.

For the log-probit model, the human average lifetime dose D_H is derived from the animal dose D as follows:

$$D_H = D \left(\frac{0.3\ kg}{70\ kg}\right)^{1/3} \qquad = 0.035\ mg/kg/day$$

$$= 2.5\ mg/day.$$

Excess probability of response at dose x is,

$$\begin{aligned} P(x) &= (19/121 - 2/47)/(1 - 2/47) = 0.12 \\ &= \Phi\,(A + \log_{10} D_H) \\ &= \Phi\,(A + 0.40), \\ -1.18 &= A + 0.40, \\ A &= 1.6. \end{aligned}$$

Table 5-10 gives the predicted lifetime risk per capita due to absorption of nickel carbonyl into the blood. The two models give roughly similar

TABLE 5-10. PREDICTED EXCESS LIFETIME PER CAPITA RISK DUE TO NICKEL CARBONYL ABSORBED DOSE

	Absorbed Dose (mg/day)						
	0.00001	0.0001	0.001	0.01	0.1	1	10
Linear Model B_H = 0.05 per(mg/day)	5×10^{-7}	5×10^{-6}	5×10^{-5}	5×10^{-4}	5×10^{-3}	5×10^{-2}	0.4
Log-Probit Model A_H = -1.6	off scale	off scale	2×10^{-6}	1.6×10^{-4}	5×10^{-3}	6×10^{-2}	0.3

Source: Arthur D. Little, Inc.

predictions relative to the large uncertainties in the assumptions used in the calculations. It should be remembered that this analysis only applies to absorbed nickel carbonyl (by inhalation or the intravenous route) and does not apply for any other nickel compound by any other route.

5.1.6.4 Nickel Subsulfide

For nickel subsulfide the best carcinogenicity data (amenable to dose-response extrapolation) currently available are from a study on Fischer 344 rats exposed to nickel subsulfide via inhalation (Ottolenghi et al. 1974). The data selected for analysis are listed in Table 5-11. The data used were the incidences of lung neoplasms in test and control rats. The human equivalent exposure was not determined using a human-to-animal surface area ratio, such as is the normal procedure, since inhalation minute-volume is approximately proportional to body surface area. Thus, dose equivalence between humans and experimental animals is roughly attained on the basis of body surface area when air is breathed at the same concentration of the aerosol. This assumes a similar disposition and retention of particulates, which is probably not a valid assumption.

In keeping with EPA guidelines (U.S. EPA 1980a) it was assumed that human lifetime response is related to total amount of exposure over the rat lifetime. Assuming 104 weeks for the average rat lifetime, the average human lifetime exposure D_H is given by

$$D_H\ (\mathrm{mg/m^3}) = (1\ \mathrm{mg/m^3}) \times \left[\frac{(6\ \mathrm{hr/day}) \times 5\ \mathrm{day/wk}) \times (78\ \mathrm{wk})}{(24\ \mathrm{hr/day}) \times (7\ \mathrm{day/wk}) \times (104\ \mathrm{wk})}\right]$$

$$= 0.13\ \mathrm{mg/m^3}.$$

From this, and the data in Table 5-11, the one-hit parameter B is given by

$$B = \frac{1}{(.13\ \mathrm{mg/m^3})}\ \ln\left(\frac{1 - 2/215}{1 - 29/208}\right)$$

$$\cong 1.1\ \text{per mg/m}^3$$

For the log probit model,

$$\left(\frac{29}{208} - \frac{2}{215}\right) = \Phi\ (A + \log_{10}\ [.13\ \mathrm{mg/m^3}]),$$

so that the probit intercept $A = -0.23$. The multi-stage model was not applied because insufficient data.

Table 5-12 displays estimates of lifetime human risk based on these values of B and A. Risk estimates are shown for exposure levels ranging from 1 ng/m^3 to 1 mg/m^3. As expected, the gap between the estimates is larger in the low-dose region; thus the model chosen may contribute a substantial degree of uncertainty concerning the actual carcinogenic effects of nickel subsulfide at low levels of exposure. However, much larger contributions to uncertainty stem from extrapolation from rat to human and estimation of the equivalent daily exposure from a short-duration exposure.

TABLE 5-11. CARCINOGENIC RESPONSE IN FISCHER 344 RATS INHALING NICKEL SUBSULFIDE

Rat Exposure	Equivalent Human Exposure (mg/m^3)	Response	Percentage (%)	Percentage Excess Over Controls (%)
1 mg/m^3, 6 hr /day, 5 day/week, 78 weeks	0.13	29/208	14	13
0 mg/m^3	0	2/215	1	-

Source: Based on data from Ottolenghi *et al*. (1974)

TABLE 5-12. PREDICTED EXCESS LIFETIME PER-CAPITA RISK DUE TO NICKEL SUBSULFIDE INHALATION

Air Concentration (mg/m^3)

	0.000001	0.00001	0.0001	0.001	0.01	0.1	1
Linear Model B = 1.1 per mg/m^3	1×10^{-6}	1×10^{-5}	1×10^{-4}	1×10^{-3}	1×10^{-2}	1×10^{-1}	7×10^{-1}
Log-Probit Model A = -0.23	off scale	2×10^{-7}	1.2×10^{-5}	6.4×10^{-4}	1.3×10^{-2}	1.1×10^{-1}	4×10^{-1}

Source: Arthur D. Little, Inc.

It should be remembered that the results given here apply only to nickel subsulfide by inhalation, not to pure nickel or to any other nickel compound by any other route.

5.2 EXPOSURE

5.2.1 Introduction

Nickel is ubiquitous in the contemporary human environment such that humans are almost inevitably exposed to nickel in its various chemical forms by ingestion, inhalation, and dermal contact. It has been emphasized in the preceding sections on human health effects that effects depend on route of exposure and species of nickel. However, most data on human exposure do not distinguish among the various nickel compounds. In this section, the routes of exposure are discussed separately, and, where available, speciation is indicated.

Throughout this chapter, nickel concentrations are reported in drinking water; food; urban, industrial, and non-urban air; manmade objects; and cigarettes.

In this section, the routes of man's exposure are identified and, where possible, quantified. These routes are exposure through ingestion, exposure through inhalation, and percutaneous exposure.

5.2.2 Exposure Routes

5.2.2.1 Exposure Through Ingestion

Man may ingest nickel that is in drinking water or food, or which is added to them either during the course of processing as a result of contact with nickel-bearing containers, utensils, or equipment.

Nickel has been detected in groundwater and well water and in finished drinking water supplies at low concentrations. The Community Water Supply Study sampled and analyzed drinking water in 969 systems serving approximately 18,200,000 persons[1] (NAS 1975) The results of the analysis for nickel are presented in Table 5-13; the average nickel concentration found in these water supplies was 4.8 mg/l.

Other studies of tap water and well water in the United States found average concentrations of nickel in the range of 2.3 μg/l to 13.0 μg/l, as shown in Table 5-14. All means reported here were below the established water quality criterion of 13.4 μg/l. For comparsion, the mean nickel concentration in drinking water in the heavily industrial city of Sudbury, Ontario is 200 μg/l, however, this is not to be considered at all typical of concentrations in water supplies in the United States.

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[1] This study took place in 1963 at which time there were 19,236 public water supply systems serving approximately 150 million persons in the United States.

TABLE 5-13. NICKEL IN DRINKING WATER SUPPLY SYSTEMS IN THE UNITED STATES

Nickel Content (μg/l)	Samples	Frequency of Detection (%)
<0.9	543	21.69
1 - 5	1082	43.22
6 - 10	640	25.57
11 - 15	167	6.68
16 - 20	46	1.84
21 - 25	14	0.56
26 - 30	4	0.16
31 - 35	2	0.08
36 - 40	1	0.04
41 - 45	1	0.04
46 - 50	1	0.04
51 - 55	1	0.04
75	1	0.04
Total	2503	100.00

Average concentration 4.8 μg/liter

Note: Covers all 969 water supplies in eight metropolitan areas and one state.

Source: NAS (1975)

TABLE 5-14. NICKEL LEVELS IN DRINKING WATER

Survey	Mean (µg/l)	Maximum (µg/l)	Number of Systems Samples	Reference
Tap Water				
8 Metropolitan Areas (1969-1970)	4.8	75	969	NAS (1975)
10 Largest U.S. Cities (1972)	2.3-13.0[a]	-	-	Dufor and Becker (1964)
Hartford, CT	1.1	1.5	-	McNeely *et al.* (1972)
Sudbury, Ontario	200	264	-	McNeely *et al.* (1972)
Well Water, typical	10	50	-	U.S. EPA 1980b
Well Water, maximum in Ohio River Basin 1978 and 1979		31,700[b]		U.S. EPA 1980b

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[a] New York City; Philadelphia; Chicago; Los Angeles; Detroit; Houston; Baltimore; Dallas; San Diego; and San Antonio.

[b] This value was reported in only one sample and is not considered representative of the maximum nickel concentrations in U.S. drinking waters.

Typical maximum concentrations reported in the literature (NAS 1975) and in the STORET Water Quality System (U.S. EPA 1980b) were in the range of 1.5 μg/l to 75 μg/l. Exceptionally high concentrations were reported in certain well samples in the Ohio River Basin on isolated occasions in 1978 and 1979; these were 31,200 μg/l and 31,700 μg/l (U.S. EPA 1980). There is no information available on the number of persons served.

It has been estimated that man drinks an average of 2 liters of water per day. The daily intake contributed by drinking water to ingested nickel would be an average of 4.6 μg to 26 μg per day, with a typical maximum contribution in the United States of less than 150 μg/day.

Nickel is found in food as a result of its occurrence in the environmental media through man's activities and natural phenomena. Nickel occurs naturally in soil and is deposited through atmospheric fallout and waste disposal to land; nickel occurs in water due to erosion of rocks and soils and also from atmospheric fallout. The nickel in soil and water is taken up by most organisms and is passed from zooplankton, phytoplankton, and plants to higher forms of life.

The nickel levels found in harvested crops are dependent primarily on the crop and less on the concentration of nickel in soil and soil characteristics. Leafy vegetables, such as lettuce and grass-like plants, usually contain the highest nickel levels of crops. There does not appear to be any particular affinity of nickel for fruits, seeds, or other high lipid plant constituents.

In most crops grown in sludge-amended soils, nickel concentrations do not usually exceed 4 μg/g. Lettuce and wheat tend to have higher levels, on the order of 10-200 μg/g (see Table 4-14 in Chapter 4.0). Unusually high concentrations were measured under laboratory conditions. Under low pH conditions, which could easily develop in unmanaged sludge-treated sites, concentrations increase dramatically to levels as high as 1150 μg/g in lettuce and 4000 μg/g in allysum (a forage crop). No field study of a sludge-amended plot found comparable levels. Until such time as these results are verified in the field, these concentrations cannot be considered representative of foods grown in sludge-amended soils. However it is likely that the concentration of nickel will be higher in sludge-treated soils than in non-treated soils. The behavior of nickel in plants and organisms is more fully discussed in Section 4.4 - Biological Fate.

Nickel occurs as a trace element in many foods that man consumes. The nickel concentration is reportedly high in green leafy vegetables, grains, tea, herring, and oysters and, as noted above, is likely to be higher in crops treated with sewage sludge (Schroeder et al. 1961, Underwood 1971). A sample of foods containing nickel and associated concentrations is presented in Table 5-15. A more detailed analysis of nickel in foods is found in Table 4-14.

TABLE 5-15. NICKEL CONCENTRATION IN VARIOUS FOODS

FOOD GROUP	AVERAGE CONCENTRATION NICKEL (μg/g)
Dairy	0.00-0.03
Meat, Fish, Poultry	0.00-4.50
Grains	0.00-6.45
Potatoes	0.56
Leafy Vegetables	0.14-1.14
Legume Vegtables	0.17-2.59
Garden Fruits	0.03-0.33
Root Vegetables	0.37-1.94
Fruits	0.00-0.34
Oils and Fats	0.00-1.14
Sugars	0.03
Beverages	0.00-7.60

SOURCE: Schroeder _et al_. (1961)

Nickel in food due to leaching from processing equipment is another source of ingested nickel. Depending on the pH of the food, there is a potential for corrosion of nickel-alloy vessels during use. Many stainless steels (most containing nickel) have been shown to lack corrosion resistance (NAS 1975). Equipment used in milling flour and wheats is likely to add nickel to end-products such as breads.

There is little information available on the chemistry of nickel in foods. It is therefore impossible to realistically determine the bioavailability and biotoxicity of nickel in foods. However, the nickel contribution in foods eaten by man has been calculated.

Oral intakes of nickel as a result of food consumption has been determined by several studies and is summarized in Table 5-16. The average amount of nickel consumed in the daily diet ranged from 165 μg to 900 μg. There is apparent variation between the diet of males and females, the latter being higher in nickel, as indicated by Tipton and coworkers (Tipton *et al.* 1966). While the Tipton study was an isolated study of only one male and one female, it provided thorough documentation and was included as a basis for comparison.

5.2.2.2 Exposure Through Inhalation

Man may be exposed by inhalation to nickel in ambient air and in cigarette smoke. Nickel occurs in the atmosphere as a result of industrial activity, combustion of fossil fuels, or other human activities in the urban environment. In the rural environment, nickel occurs in the air largely as a result of wind erosion of nickel-bearing soils. The species of nickel in ambient air have not been identified. Nickel in cigarette smoke, on the other hand, is believed to be mostly nickel carbonyl. Because of this distinction, the two inhalation exposure routes are discussed separately.

Nickel is commonly detected in the atmosphere surrounding urban areas. Sources of nickel include combustion of petroleum fuels, which contain up to 50 mg/l nickel (Acurex 1980); combustion of coal, the ash of which contains 3 to 10,000 mg/kg nickel (Schroeder *et al.* 1970); and particulates from the exhausts of non-diesel vehicles, which contain 500 to 10,000 mg/kg nickel (Schroeder *et al.* 1970). The concentration that this corresponds to in air has not been determined.

There are several studies which present concentrations of nickel in urban air and these are summarized in Table 5-17. In a study of 58 cities by Schroeder *et al.* (1961), the range of nickel concentrations in urban air was 1 to 118 ng/m^3, with two-thirds of the locations sampled being less than 20 ng/m^3.

A seasonal variation in nickel concentration in the urban environment has been determined in one study reported by the National Academy of Science (1975). The results are shown in Table 5-18. Nickel was

TABLE 5-16. NICKEL IN THE HUMAN DIET

COMPARATIVE DIET	AVERAGE NICKEL IN THE DIET (µg/day)	REFERENCE
2300-Calorie Diet	700-900	Schroeder *et al.* (1961)
Institutional Diet in United States	472	Schroeder *et al.* (1961)
Institutional Diet in United States	165	Myron *et al.* (1961)
Institutional Diet Children 9-12 years old	451	Murthy *et al.* (1973)
Dietary Analysis of Husband and Wife:		
Male	170	Tipton *et al.* (1966)
Female	330	Tipton *et al.* (1966)
American Adults	500	Louria *et al.* (1972)

TABLE 5-17. NICKEL IN URBAN AIR

Description	Range (ng/m^3)	Mean When Available (ng/m^3)	Reference
Ten Cities Studied			
Year-Round	30-120		Schroeder *et al.* (1970)
Colder Months		44	Schroeder *et al.* (1970)
Warmer Months		26	Schroeder *et al.* (1970)
Urban Air			
56 Cities Detected of 58 sampled	1-118		Schroeder *et al.* (1970)
Urban Air	up to 690	32	Sullivan (1969)
Boston Air	-	112	NAS (1975)
East Chicago Air	-	132	NAS (1975)
Philadelphia Air		78	NAS (1965)

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[a] Cities include New York City; Rochester, NY; Bayonne, NJ; Portland, OR; Somerville, MA; New Haven, Hartford, and Bridgeport, CT; Bakersfield, Burbank, and San Bernadino, CA; Baltimore, MD.

TABLE 5-18. SEASONAL VARIATION OF NICKEL IN AMBIENT AIR

	Urban Air (ng/m^3)	Non-Urban Air (ng/m^3)
All Year	21	6
Fall and Winter	25	6
Spring and Summer	17	6

Source: NAS (1975)

detected at concentrations almost 50% higher in the fall and winter months than in the spring and summer months. Nickel in the rural environment did not appear to vary between seasons.

Nickel is contributed to the general urban environment as a result of coal and petroleum combustion for power generation and utilization of petroleum for space heating. The population in the vicinity of these point sources is exposed to greater concentrations of atmospheric nickel. Samples of stacks from coal-fired power plants indicate that nickel concentrations range from 13-65 $\mu g/m^3$ (Lisk 1972). The same study sampled petroleum-burning plant emissions and determined nearby atmospheric concentrations of 63 to 447 $\mu g/m^3$.

The associated atmospheric nickel concentrations to which the nearby populations are exposed would clearly be significantly lower as the particles disperse through the air, the heavier ones falling out on the land. Sampling data were not available to identify the species of nickel resulting from these emissions or to identify the associated concentrations.

Non-urban atmospheric concentrations of nickel are clearly lower than in the urban and industrial environments. The mean concentration of nickel reported in a study of 47 non-urban areas by the National Air Surveillance Networks (NASN) was 6 ng/m^3 (NAS 1975). Other studies reported (NAS 1975) concur with the NASN results that the ratio of nickel in urban air to that in non-urban air is typically 2:1.

To summarize inhalation exposure through ambient air, nickel concentrations range from 0.6 ng/m^3 to 690 ng/m^3 in most environments and are possibly higher near industrial emitters of nickel; these levels are shown in Table 5-19. Although average inhalation rates have been determined (1.8 m^3/hr), without identifying the species of nickel inhaled, its absorption rate and location cannot be determined. It is difficult to estimate the actual amounts of nickel absorbed via inhalation without data on speciation, particle size, and actual determination of respiration retention for each species.

Nickel is found in the leaves of tobacco products used for cigarettes. Stahly (1973) reported that nickel carbonyl occurs in cigarette smoke at concentrations of 0.35-1.8 μg Ni per liter of smoke, which is approximately 1.5 μg nickel carbonyl per cigarette (assuming 14 puffs of 36 milliliters each). Most of the nickel contained in an average cigarette remains in the ashes, butt, and filter. These measurements are consistent with the hypothesis that the nickel carbonyl is formed in the cooler zones of the cigarette behind the combustion zone by combining the nickel in the tobacco, the paper, and the CO produced from the burning tobacco. Nickel was removed from tobacco by passing CO through it at temperatures between 20 and 100°C. The inhalation retention for nickel carbonyl is uncertain, but, assuming a retention of 50%, a one-pack-a-day smoker may absorb 15 μg/day or about 5 mg/yr

TABLE 5-19. NICKEL CONCENTRATIONS IN AMBIENT AIR

	Minimum (ng/m^3)	Maximum (ng/m^3)	Mean (ng/m^3)	Reference
Non-Urban Air	0.6	12.0	-	See Section 4.5.5.3
Non-Urban Air	-	-	6.0	NAS (1975)
Urban Air	1.0	690.0	-	See Table 5-17
At the Point of Emission of Combustion Plants				
Coal Combustion	12,900[a]	65,000[a]	-	Lisk (1972)
Petroleum Combustion	63,000[a]	447,000[a]		Lisk (1972)

[a] Note: Associated atmospheric levels beyond the stacks will be significantly lower.

of nickel carbonyl. The actual amount of nickel carbonyl absorbed when smoking would also depend on puffing rates and brand of tobacco. Stahly (1973) suggests there may be practical ways to remove nickel from tobacco products.

5.2.2.3 Cutaneous Exposure

The use of nickel-containing commodities which permit cutaneous exposure to nickel is legion and was estimated to be increasing by about 10% per year (NAS 1975). The major sources of environmental cutaneous exposure to nickel are jewelry, coinage, clothing fasteners, tools, cooking utensils, stainless steel kitchens, and detergents. At issue is which sources are most likely to be involved in the sensitization of people to nickel and which sources may only be involved in continued sensitivity reactions.

There seems little doubt that sensitization arises in susceptible individuals due to exposure to coinage (especially cashiers), jewelry, and nickel-plated garment fasteners. More controversial is the role of nickel in detergents in causing or even eliciting a response in sensitive individuals. Studies cited by NAS (1975) reported nickel content of detergents of less than 10 mg/kg, which levels were thought not adequate to produce sensitization. Exposure to nickel from stainless steel kitchens has not been investigated carefully for its potential to produce sensitization.

Fischer (1967) has stated that sweating has a profound affect on the degree of dermatitis and is required for sensitization to nickel. It is hypothesized that nickel combines or is solubilized by sweat, diffuses into sweat ducts and hair ostia, and subsequently into dermis, where it combines with components of the skin and soluble proteins. The resultant nickel "complex" is an antigen which stimulates an immunological response (NAS 1975). Further research is necessary to clarify details of this hypothesized scenario.

An association between nickel in ambient air or nickel ingestion and contact sensitivity has not been suggested. Two cases of Loffler's syndrome (pulmonary eosinophilic) have been reported (Sunderman and Sunderman 1961) which were each associated with exposure to nickel carbonyl. One of the individuals was subjected to a nickel patch-test and found to be very sensitive.

5.2.3 Summary

Nickel exposure through ingestion of drinking water does not appear to be a significant route due to the generally low concentrations of the metal found in well waters and treated drinking water systems. Except in rare instances, drinking water concentrations were below the established Water Quality Criterion of 13.4 ug/l. Nickel exposure through oral intake of food typically contributes 100 μg to 900 μg to the daily diet, however, nothing is known about its chemical form. Nickel in ambient air occurs in fairly low concentrations ranging from 0.6 ng/m^3 to 690 ng/m^3 and most frequently between 100 ng/m^3 to 200 ng/m^3. In areas near intense industrial activity with associated high nickel emissions, the nickel concentrations are higher but speciation is unknown. Cigarette smoking may contribute 15 μg/day of nickel carbonyl to the average one-pack-a-day smoker. Finally, percutaneous exposure occurs as a result of contact with nickel-bearing objects (e.g., stainless steel kitchenware, jewelry). Upon repeated contact with such objects, the skin of some individuals may become sensitized, however more study is needed on the grade of alloy from which these objects are made and the associated releases of nickel.

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6.0 EFFECTS AND EXPOSURE -- AQUATIC ORGANISMS

In this chapter, the effects of nickel on aquatic organisms are considered within the context of the available exposure data.

6.1 EFFECTS

6.1.1 Introduction

This section provides information about the levels of nickel at which the physiologic processes and normal behavior of aquatic organisms are disrupted.

Nickel is a common component of natural waters and may be found in "unpolluted" waters at levels less than 1 µg/l (U.S. EPA 1980b). It is possible that nickel is an essential element to biota in trace amounts (probably low µg/l range or lower), but the threshold of toxic effects to freshwater organisms is in the range of 1 µg/l to 10 µg/l. In an aqueous environment, nickel may exist, albeit infrequently, in the very insoluble elemental form. The more common form in waters is the free divalent nickel ion (Ni^{++}), resulting from one of the nickel salts (e.g., nickel chloride, nickel sulfate, nickel ammonium sulfate) or one of many other nickel compounds or complexes. In toxicity test systems, with low concentrations of suspended solids and dissolved organic matter, the most prevalent form of nickel is the Ni^{++} free form. Nickel salts are very soluble in distilled water; however, in natural waters their solubility varies with such water quality parameters as pH, hardness, and alkalinity. The solubility of nickel salts in general decreases with increasing water hardness, a factor which greatly affects the toxicity of nickel to aquatic organisms under both natural and experimental conditions. Toxicity tests have shown that as water hardness increases, toxicity of nickel to aquatic organisms decreased (U.S. EPA 1980a).

Although more than 180 organonickel compounds and nickel complexes are commercially available in the United States, studies to determine the mechanisms of toxicity have been conducted on only a few of them, and most of these studies have been performed on laboratory mammals. Nickel in the elemental form is considered not to be very toxic, and is generally passed through systems, such as sewage treatment plants and individual organisms, essentially unchanged. Nickel salts have been observed to be highly toxic to laboratory mammals when injected, but when orally ingested more than 90% of the nickel was excreted (NAS 1975). From studies conducted by Schweiger (1957) of the acute effects of nickel (Ni^{++}) on several riverine fish species, it was observed that mortality was caused by suffocation, with paralysis preceding death. Histological examination showed respiratory gill obstruction by mucous matter expelled from the cells.

6.1.2 Freshwater Organisms

6.1.2.1 Acute Effects

The acute effects of nickel have been tested in numerous freshwater organisms. Many of the organisms were studied under varying conditions of water hardness (mg/l as $CaCO_3$). Water hardness greatly affects the toxicity of nickel to biota and, in general, as hardness increases, an organism's resistance to toxicity increases. This toxicity difference between hard and soft water is due to the fact that absorption of trace metals from the environment by biota is inversely related to the concentration of calcium (Hutchinson and Collins 1978). Natural levels of nickel in freshwater have been found to range from 0.003 mg/l to 0.086 mg/l (U.S. EPA 1980b). Of the freshwater fish tested, the most sensitive species is the fathead minnow (*Pimphales promelas*); LC_{50}[1] values in soft water were 3-5.1 mg/l. Hard water toxicity values were much higher, in the 25-45 mg/l range. The goldfish (*Carossius auratus*) and guppy (*Lebistes reticulatus*) were also sensitive to nickel in the range of 4-10 mg/l in soft water. Toxicity data for several freshwater fish are summarized in Table 6-1.

Of the freshwater invertebrates studied, the zooplankton (cladocera, copepod, and rotifers) and two aquatic insects were killed by nickel at somewhat lower concentrations than were the most sensitive fish species (LC_{50} range of 1-4 mg/l). The snail *Amnicola* spp., the bristleworm, and several other aquatic insects had LC_{50} values of 14.3, 14.1, and 28-33 mg/l, respectively. The available data for acute toxicity to freshwater invertebrates are summarized in Table 6-2.

Several freshwater algae species have been studied for nickel toxicity. Reduced growth occurred in four species tested at concentrations in the range of 0.100-0.700 mg/l (see Table 6-3). In mixed algae populations, a decrease in diatom diversity and a population shift to blue-green algae was observed in 0.002-0.0086 mg/l of nickel (U.S. EPA 1980a).

Freshwater toxicity data for several other nickel compounds are summarized in Table 6-4.

6.1.2.2 Chronic Effects

Chronic or sublethal effects of a toxic substance in aquatic organisms are generally determined by observing effects such as loss of equilibrium, melanization, narcosis, swollen hemorrhaging gills, and changes in reproductive or feeding habits or capabilities.

Fathead minnows exposed continuously from age 6 weeks until they spawned to a concentration of 0.73 mg/l $NiCl_2$ showed no effect on growth

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[1] LC_{50} is the concentration that is lethal to 50% of the test organisms.

TABLE 6-1. ACUTE TOXICITY OF NICKEL - FRESHWATER FISH

Organism	Bioassay[a] Method	Hardness (mg/l as CaCO$_3$)	Time (hrs)	LC$_{50}$ (mg/l)	Reference
American eel *Anguilla rostrata*	S	55	96	13.0	Rehwoldt *et al.* (1972)
Brook Trout *Salvelinus tontinalis*	S	42	48	53.9	Willford (1966)
Rainbow Trout *Salmo gairdneri*	S	240	48	32.0	Brown and Dalton (1970)
Rainbow Trout *Salmo gairdneri*	S	42	48	35.7	Willford (1966)
Lake Trout *Salvelinus namaycush*	S	42	48	16.7	Willford (1966)
Goldfish *Carassius auratus*	S	20	96	9.8	Pickering and Henderson (1966)
Fatheadminnow *Pimephales promelas*	S	210	96	27.0	Pickering (1974)
Fathead minnow *Pimephales promelas*	S	20	96	5.2	Pickering and Henderson (1966)
Fatheadminnow *Pimephales promelas*	S	360	96	44.5	Pickering and Henderson (1966)
Fathead minnow *Pimephales promelas*	FT	29	96	2.9	Lind *et al.* (no date)
Carp *Cyprinus carpio*	S	55	96	10.4	Rehwoldt *et al.* (1972)
Channel catfish *Ictaluris punctatas*	S	42	48	36.8	Willford (1966)
Banded killifish *Fundulus diaphanus*	S	55	96	46.1	Rehwoldt *et al.* (1972)

TABLE 6-1. ACUTE TOXICITY OF NICKEL - FRESHWATER FISH (CONTINUED)

Organism	Bioassay Method	Hardness (mg/l as $CaCO_3$	Time (hrs)	LC_{50} (mg/l)	Reference
Guppy Lebistes reticulatus	S	20	96	4.4	Pickering and Henderson (1966)
Rock bass Ambloplites rupestris	FT	26	96	2.5	Lind et al. (no date)
Striped bass Roccus saxatilius	S	53	96	6.2	Rehwoldt et al. (1971)
Pumpkinseed Lepomis gibbosus	S	55	96	8.0	Rehwoldt et al. (1972)
Bluegill Lepomis macrochirus	S	20	96	5.2	Pickering and Henderson (1966)
Bluegill Lepomis macrochirus	S	360	96	39.6	Pickering and Henderson (1966)
Bluegill Lepomis macrochirus	S	42	48	110.4	Willford (1966)
White perch Roccus Americanus	S	53	96	13.6	Rehwoldt et al. (1971)

[a] Bioassay Method:

S = Static; test organisms are exposed to a single concentration of the pollutant in a fixed volume of water in order to simulate an accidental exposure.

FT = Flow through; fixed concentration in continually flowing water to simulate a constant source of pollutant (e.g. a discharge).

TABLE 6-2. ACUTE TOXICITY OF NICKEL - FRESHWATER INVERTEBRATES

Organism	Bioassay[a] Method	Hardness (mg/l $CaCO_3$)	Time (hrs)	LC_{50} (mg/l)	Reference
Rotifer *Philodina acuticornus*	R	25	96	2.9	Buikema *et al.* (1974)
Bristle worm *Nais* sp	S	50	96	14.1	Rehwoldt *et al.*(1973)
Snail (egg) *Amnicola* sp.	S	50	96	11.4	Rehwoldt *et al.* (1973)
Snail (adult) *Amnicola* sp.	S	50	96	14.3	Rehwoldt *et al.* (1973)
Cladoceran *Daphnia hyalina*	S	-	48	1.1	Baudoin and Scoppa (1974)
Cladoceran *Daphnia magna*	S	45	48	0.5	Biesinger and Christensen (1972)
Cladoceran *Daphnia pulicaria*	R	29	48	0.7	Lind *et al.* (no date)
Cladoceran *Daphnia pulicaria*	R	244	48	3.8	Lind *et al.* (no date)
Copepod *Cyclops abyssorum*	S	-	48	15	Baudoin and Scoppa (1976)
Copepod *Eudiaptomus padanus*	S	-	48	3.6	Baudoin and Scoppa (1976)
Scud *Gammarus* sp.	S	50	96	13	Rehwoldt *et al.* (1973)
Mayfly *Ephemerella subvaria*	S	42	96	4.0	Warnick and Bell (1969)
Stonefly *Acroneuria lycorias*	S	50	96	33.5	Warnick and Bell (1969)
Damselfly (unidentified)	S	50	96	21.2	Rehwoldt *et al.* (1973)
Midge *Chironomus* sp.	S	50	96	8.6	Rehwoldt *et al.* (1973)
Caddisfly (unidentified)	S	50	96	30.2	Rehwoldt *et al.* (1973)

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[a] Bioassay Method:

R = Renewal; variation of a static test with repeated exposure.
S = Static

TABLE 6-3. EFFECTS OF NICKEL ON FRESHWATER PLANTS

Organism	Effect	Concentration (mg/l)	Reference
Alga *Chlamydomonas eugametos*	Reduced growth	0.7	Hutchinson (1973)
Alga *Chlorella vulgaris*	Reduced growth	0.5	Hutchinson (1973)
Alga *Haematococcus capensis*	Reduced growth	0.3	Hutchinson (1973)
Alga *Scenedesmus acuminata*	Reduced growth	0.5	Hutchinson and Stokes (1975)
Alga *Scenedesmus acuminata*	Reduced growth	0.1	Hutchinson (1973)

TABLE 6-4. FRESHWATER TOXICITY - OTHER NICKEL COMPOUNDS

Nickel chloride

Organism	Water Condition	Time (hrs)	Concentration (mg/l)	Effect
Gold fish *Carassius auratus*	-	200	4.5	Lethal
Guppy *Lebistes reticulatus*	soft	96	4.45	TL_m^a
Fathead minnow *Dimephales promelas*	soft	96	4.0	TL_m
Fathead minnow *Pimephales promelas*	hard	96	24	TL_m
Daphnia magna	-	-	6.0 (As N:)	Toxic threshold
Bluegill *Lepomis macrochirus*	soft	96	5.18	
Bluegill *Lepomis macrochirus*	hard	96	39.6	TL_m
E. coli	-	-	0.1	threshold concentration

Nickel Sulfate

Organism	Water Condition	Time (hrs)	Concentration (mg/l)	Effect
Stickelback		49	50	Lethal
Rainbow Trout *Salmo gairdneri*		48	160	TL_m
Brown Trout *Salmo trutta*		48	270	TL_m
Brook Trout *Salvelinus fontinalis*		48	242	TL_m
Lake Trout *Salvelinus mamycush*		48	75	TL_m
Chanel Catifish *Ictalurus punctatus*		48	165	TL_m
Mayfly *Ephemerella* sp.				
Stonefly *Acroneuria lycorias*		96	33.5	TL_m

TABLE 6-4. FRESHWATER TOXICITY - OTHER NICKEL COMPOUNDS (CONTINUED)

Nickel Ammonium Sulfate

Organism	Concentration (mg/l)	Effect
Daphnia magna	6(Ni)	Deleterious Effect
E. Coli	0.1	Toxic Threshold
Scenedesmus	0.09	Toxic Threshold

Nickel Nitrate

Organism	Concentration (mg/l)	Effect
Stickleback	2.44	Threshold Concentration
Stickleback	1.5	Lethal Concentration(96hr)
Stickleback	0.8	Lethal Concentration(24hg)

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[a] TL_m = median tolerance limits.

Source: U.S. EPA (no date)

and survival, but a significant reduction in the number of eggs per spawning incidence and on the hatchability of the eggs was observed (Blaylock and Frank 1979).

In experiments with carp (Cyprinus carpio) eggs and larvae, there was no effect on hatchability of the eggs in concentrations of nickel up to 4 mg/l. At 6 mg/l, only 50% of the eggs hatched, with no further decrease in percentage hatched through 7 mg/l nickel. At concentrations greater than 7 mg/l, embryonic development continued through the eyed-embryo stage, but the number of eggs hatched decreased until at 10 mg/l only 3 larvae, which were abnormal, hatched from 414 eggs. At concentrations greater than 30 mg/l, no embryonic development was observed (Blaylock and Frank 1979).

6.1.3 Marine Organisms

Toxicity data for marine biota are not extensive, and there is even less data for fish than for invertebrates. Background concentrations of nickel in sea water were found to be approximately 0.0054 mg/l (U.S. EPA 1980b). The most sensitive fish species tested was the Atlantic Silverside, LC_{50} of 14.6 mg/l. Other values are 33 mg/l for the winter flounder, and 350 mg/l (96 hr) for the Mummichog.

Data for several marine invertebrates are summarized in Tables 6-5 and 6-6. Toxicity values for these benthic organisms were in the range of 25 mg/l to 700 mg/l, the most sensitive being the hermit crab (Pagurus longicarpus). The data for these invertebrates show that in almost every instance there was a marked and progressive decline in LC values between 24 and 168 hours (Eisler and Hennecky 1977). Toxicity levels for all the organisms tested were confined to a relatively narrow range.

In studies of marine organisms used as human food products it was found that Pacific Coho Salmon (Onchorhynrhus kisutch) contained three times the concentration of nickel than that found in other fish tested, and twice the level found in mollusks. Lobsters were found to contain higher levels of nickel than several mammalian species tested (NAS 1975).

6.1.4 Factors Affecting Toxicity

The effects of water hardness on the toxicity of nickel, primarily in freshwater systems where hardness values can vary substantially, was previously discussed. Other factors that affect nickel toxicity are not as well studied. Eisler (1977) studied the effects of mixed metal solutions (Ni, Mn, Zn, Pb, Cu, Cd) on a marine bivalve mollusk (Mya arenaria). It was found that these clams showed increasing resistance to metals with decreasing ambient water temperature. Marine bivalves

TABLE 6-5. ACUTE TOXICITY OF NICKEL - ESTUARINE MACROINVERTEBRATES

Organism	Time Interval (hr)	(LC_{50} mg/l)
Starfish	24	270
Asterias forbesi	96	150
	168	13
Mudsnail	24	540
Nassarius obsoletus	96	72
	168	16
Sandworm	24	320
Nereis virens	96	25
	168	25
Hermit crab	24	130
Pagurus longicarpus	96	47
	168	30
Softshell clam	24	700
Mya arenaria	96	320
	168	112

Source: Eisler and Hennecky (1977).

TABLE 6-6. TOXICITY OF NICKEL SULFATE - MARINE MACROINVERTEBRATES

Organism	Hours	LC_{50} (mg/l)
Prawn	48	13.9
Shrimp	48	125
Cockle	48	7500
Crab	48	255
Oyster	48	100-150

Source: U.S. EPA (no date)

are known to exhibit consistent and measurable changes in content of selected metals (including nickel) with increasing growth, changing seasons, and as a reflection of the metal content of the sediment substrate and sediment interstitial waters (Eisler 1977). In studies with rainbow trout, however, it was found that temperature did not affect toxicity of nickel (Hughes et al. 1979).

6.1.5 Conclusions

According to the literature surveyed, the lowest concentration of nickel at which effects have been observed in aquatic organisms is 0.1 mg/l, which caused reduced growth in algae. Levels above 1 mg/l begin to cause acutely toxic effects to a variety of aquatic organisms, including freshwater fish and zooplankton, and to several aquatic insects. Data for marine organisms are not extensive, but that which is available shows that salt waterbiota, both fish and invertebrates, are less sensitive to nickel than are freshwater organisms. Sublethal effects on development of carp eggs and embryos also occur at concentrations greater than 10 mg/l. The most resistant organisms tested were several benthic marine invertebrates, including clams, mussels, and oysters, in which mortality levels were in the range of 100 mg/l to 900 mg/l. The most sensitive marine organism tested was the Atlantic Silverside, LC_{50} of 146 mg/l.

Water hardness, as measured by $CaCO_3$ content, has a considerable effect on solubility and toxicity of nickel. This probably accounts in part for the apparent greater toxicity of nickel to freshwater biota than to marine organisms. This relationship must be kept in mind when examining toxicity data for a substance such as nickel, but unfortunately information on water hardness under experimental conditions is often not given in the literature. Information on the relationship between other water quality parameters and toxicity of nickel was unavailable.

In summary, general concentration ranges can be established at which certain effects of nickel are seen in the laboratory. These ranges are not rigidly defined, however, and may overlap as a result of differences among species, life stages, or environmental variables.

• 0.0054 -0.086 mg/l	Background levels of nickel in freshwater and salt water.
• 0.10 -0.020 g/l	Represents the detection limit in one survey for nickel in water with total dissolved solids (TDS) of 200 ug/l and 400 ug/l, respectively, (see Chapter 3.0 - Materials Balance).
• ≤1 mg/l	Values in this range reduced hatching per spawning incidence in fathead minnows exposed

	to 0.73 mg/1, but did not affect growth and survival of adults. Reduced growth in 4 algae species at 0.1-0.7 mg/1. Background levels of nickel in many fresh and salt water environments also found in this range. Several river basins, particularly the Ohio, but including the Lower Mississippi, Lake Erie, Missouri, Western Gulf, and Tennessee River, reported annual average nickel concentrations greater than 100 µg/1 for two or more years of the 10-year period of STORET data.
• 1.0 - 10 mg/1	This range includes the threshold of acute toxic effects in soft water (low $CaCO_3$ content) for several species including freshwater zooplankton (cladocera, copepods), fathead minnow, guppy, rock bass, bluegill, striped bass, and several aquatic insects. Values in this range occurred as maximum ambient levels on infrequent occasions, but in several river basins, including the Ohio (4 years), Tennessee (3 years), Upper Mississippi (3 years), Lake Michigan (2 years), Missouri (2 years), Lower Mississippi (4 years), and the Western Gulf (2 years), there were higher levels.
• 10 - 100 mg/1	Acutely toxic values for numerous organisms, including Atlantic Silverside, winter flounder, Channel catfish, Killifish, trout, pumpkinseed sunfish, copepods, and aquatic insects, are in this range; caused carp eggs not to undergo embryonic development. Lethal at 24 and 96 hours to several benthic marine invertebrates, including mudsnail, hermit crab, and sandworm. In hard water, toxic levels occur at the upper end of this range.
• 100 - 1000 mg/1	Toxic at 96 hours to several marine organisms, including starfish, softshell clam, and Mummichog. No freshwater toxicity values found in this range. Levels in this range were reported only twice, in the North Atlantic Region and the Missouri River. No exposure data for salt water was available.

6.2 EXPOSURE

6.2.1 Introduction

Nickel, the 24th most abundant element in the earth's crust, is present in surface and groundwaters as a result of weathering of minerals containing the element. Aquatic organisms are exposed to low-level natural background concentrations of nickel in freshwater and salt water environments in the range of 0.0054 mg/l to 0.086 mg/l (U.S. EPA 1980b), as well as to anthropogenic sources of nickel.

In an aqueous environment, nickel exists infrequently in the insoluble elemental form. The more common form is the free, divalent nickel ion (Ni^{++}) which results from one of the nickel salts or one of the many organonickel compounds or complexes. As a trace metal, nickel is believed to be an essential element to living organisms, but the extent to which this is true is unknown. Nickel compounds are generally very soluble in distilled water, with solubility decreasing with increasing $CaCO_3$ content (hardness).

In the water column, nickel, like many of the other trace metals, is concentrated in the colloidal portions of the dissolved solids. Compared to other substances found in water (e.g., course particulates) the colloids can carry a tremendous amount of metal. Therefore, if a stream or water body contains sufficient colloids, it can transport considerable quantities of a metal which otherwise has a low solubility.

In sediments, it is believed that nickel is sorbed onto particles and is in a form which is neither exchangeable nor readily soluble in alkaline waters, thus not available to biota (Perhac 1974).

6.2.2 Monitoring Data

This section discusses the potential for exposure of aquatic organisms to nickel in water bodies in the United States

Among the major sources of nickel emissions to the aquatic environment are secondary scrap metal processing, electroplating, smelting and refining, and battery production. Discharges to land, a small portion of which may eventually reach water via runoff or leaching, result from electroplating and mining and milling. For the most part, nickel wastes from these industries are discharged to tailing ponds, sludge lagoons, landfills, or open dumps, and not directly to surface waters. Dischargers from these industries are discussed more fully in Chapter 3.0 - Materials Balance.

Mean nickel concentrations in 1980 for 16 major U.S. river basins are given in Table 4.1 (Chapter 4.0 - Environmental Pathways). These ranged from 3 ug/l for the western Gulf of Mexico to 31 ug/l for the Ohio River. A few reports are available which studied nickel levels found in sediments and surface waters of various water bodies. Levels of nickel detected in water supplies of the 100 largest U.S. cities (1962) are cited in the National Academy of Sciences study on nickel (NAS 1975). These ranged from 0.6 ug/l to 25 ug/l. Nickel levels found in marine and freshwater environments and in sediments in the Pacific Northwest and other locations in various parts of the world are referenced in Laevastu and Thompson (1951).

Nickel content of sediment was determined for two different types of streams in Tennessee (Perhac 1974). One, the Tennessee River, is located partially in an urbanized area and flows over a mineralized streambed; the other, Joe Mill Creek, is located in a rural non-mineralized area. Sample data for these streams are provided in Section 4.5 - Monitoring Data. In general, the levels of nickel in Tennessee River sediments were substantially higher than those in Joe Mill Creek.

Nickel concentrations were also measured in surface waters and sediments of various Adirondack lakes. Nickel ranges found were 0.4 µg/l to 14.8 µg/l for surface waters 0.2 µg/g to 5 µg/g for surface sediments, and 0.1 µg/g to 2.9 µg/g for subsurface sediment (10-20 cm).

For this report, the STORET data base for the 10-year period 1970-79 was examined to ascertain aquatic exposure levels of nickel (U.S. EPA 1980b). The data revealed that the majority of nickel concentrations found in surface water from 18 reporting major river basins are in the low-to-mid µg/l range (1-500 µg/l or less). A summary of these data by year and river basin is presented in Table 6-7.

The maximum concentration found was one occurrence of 800 mg/l in 1974 in the North Atlantic Region. The distribution of percentages of observations over the entire concentration range measured are presented in Table 4-1. Over the 10-year period examined, there were numerous observations of low concentration in the range of 1-50 mg/l. During this period there were approximately 50 incidences of concentrations ranging from 1 mg/l to higher amounts. This range includes threshold levels for acute and chronic toxic effects to several aquatic organisms, including zooplankton, insects, and some fish, in soft water (see Section 6.1). River basins reporting levels greater than 1 mg/l included the North Atlantic, Tennessee, Ohio, Missouri, South Central Lower Mississippi, Lake Erie, and Lake Michigan. During some portion of the 10-year period, nearly all of the river basins reported values in the range known to cause reduced growth in freshwater algae (100-900 µg/l).

6.2.3 Conclusions

Beginning in 1972, there was a steady increase in the number of occurences of concentrations greater than 1 mg/l, with 1974 having the most reported concentrations in this range (see Table 6.7). From 1974-1979, the data for the Ohio River Basin consistently showed maximum concentrations in the 1-50 mg/l range. In addition, for all of the ranges of nickel values reported, there was a marked increase in the percentage of observations in the higher ranges (low-to-mid µg/l) over the 10-year period for all river basins. No information on the temporal persistence, areal extent, or precise source of any of the higher concentrations for any of the river basins reporting was available, nor was any other water quality information available, particularly $CaCO_3$ content, which would help in determining the availability of the nickel to biota. However, despite occasional levels in the low mg/l range and

TABLE 6-7. STORET MONITORING DATA SUMMARY

(all values in μg/l except where noted)

Year

River Basin

1970	01[a]	02	06	07	08	09	10	12	13	21	22
max	450. ug/l	270	500	340	63	21	300	100	45	6	10
min	10	0	50	1.2	0	0	100	10	6	1	0
most[b]	. 20-40	<100	50-100	<60	≤10	<20	100	100	12-45 <45	<6	10

1971	01	02	03	04	05	06	07	08	09	10	13	14	21	22
max	180 ug/l	5100	20	1000	140	130	1000	1400	110	230	100	120	38	14
min	0	0	20	0	0	0	0	0	0	30	6	10	0	11
most	<90	<100	20	.1-100	<70	<100	200-1000 and<.1	<100	<100	<230	<100	<100	0	<14

1972	01	02	03	04	05	06	07	08	09	10	11	12	13	14	17	22
max	130	690	14	510	20000 1650	110.	300.	300	510	1160 1910 } 3	130	9200 15000	20	178	10	93
min	0	0	0	0	0	.02	0	0	.01	0	75	20	10	5	10	93
most	10-100	<100	<10	<50	<100	<80	<100	<10	10-500	<100; 100- 1000 -	75, 130	<200	<20	<100	10	

1973	01	03	04	05	06	07	08	09	10	12	14	22
max	1250	45	920	480	630	1020 1200	25	12800 1080 } 5	100	720	400	17
min	0	0	1.0	0	0	0	0	9	0	0	10	11
most	<100	<45	100-900 <100	<100	<100	<100 100-70	<.4	10-1000	<100	25-700	<100	-

TABLE 6-7. STORET MONITORING DATA SUMMARIES (CONTINUED)

(all values in µg/l except where noted)

Year 1974	01	02	03	04	05	06	07	08	09	10	12	14	15	21	22
max	70	800mg/l	250	2600 1400	1600 1225	1300 4100 }9	409	170	1120 ug/l 210 mg/l }3	9240	680	450	12	24	150
min	0	0	0	5	0	0	.02	0	8	0	0	3	12	1	1.0
most	< 10.	< 100	< 50	10-1000	10- 800	10- 900	10- 400	< 70	10- 900	10- 900	10-700	10-450	12	< 24	< 50

1975	01	02	03	04	05	06	07	08	09	10	11	12	13	14	21	22
max	150	320	23	100	1300	210	620	140	650	510	400	720	37	400	8	45
min	0	1	0	5	0	0	0	0	0	0	0	20	-	10	.0	1.0
most	10-100	1-100	<10	1-100	10-430	10- 100	10- 100	2-100	2-100	10- 100	< 100	100- 700	-	10-100	< 10	< 45

1976	01	02	03	04	05	06	07	08	09	10	11	12	13	14	21	22	23
max	220	550	52	100	1200(2)	100	2700	350	500	1-12 mg/l (14values)	120	1.7 mg/l	80	180	86	30	11
min	0	0	0	3.4	0	.02	0	0	0	0	0	1	5	4	8	2	9
most	<100	1-500	1-50	3-100	100-300 <100	100	100-400 1-100	100- 300 2-100	100- 500(23) 1-100	100- 900 2-100	<100	<220	<80	<100	<86	<10	<11

1977	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	17	21	22	23
max	100	230	320	1200	975	100	910	1125	650	1085 1500	1400	230	66	700	200	130	97	82	
min	0	1	0	3.4	.02	.02	0	0	0	1.4	1.65	2.	0	16	0	52.	6	2	
most	<100	<100	100-300 <100	100- 800 < 100	100- 975 1-100	10- 100	200- 900 10-100	10- 300	2- 650	10- 850	1-100	10- 230	<66	16- 700	< 100	52- 130	<97	1-10	

TABLE 6-7. STORET MONITORING DATA SUMMARIES (CONTINUED)
(all values in μg/l except where noted)

Year

1978	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15
max	900	540	700	190	31 mg/l	2800	300	110	1 mg/l	200	140	505	500	450	250
min	1	0	0	3	0	0	0	0	0	0	0	0	1	1	0
most	100-900 10-100	<100	100-700 <100	<100	1.19-31.2mg/l (117 values), <100	<100	<100	<80	100-1000(32) 1.-100	<200	<100	100-500 1-100	<45	10-450	<25

1979	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	19	21	22
max	280	190	200	440	31.7mg/l	100	400	260	900	220	260	150	50	80	100	200	25	20
min	0	0	0	0	0	<10	0	2	0	0	0	0	0	0	0	100	0	0
most	<280	10-100	<100	<100	1.0-31.7 mg/l(141) 10-900 μg/l	<100	10-400	10-100	100-900 2-100	10-100	<100	<60	<50	<80	<10	100-200	<10	<10

[a] These numbers are River Basin Codes. See Appendix E for list of codes and name.

[b] The "most" category represents an estimation of the range(s) in which a majority of the values for that river basin occurred.

Source: U.S. EPA (1980b)

many in the range 100-500 µg/l, which has been found to cause chronic effects in algae and freshwater fish eggs, overall the levels of nickel found in streams are below 100 µg/l. No adverse effects to aquatic organisms have been found below this level. An exception to this generalization is the Ohio River Basin, which for several years showed maximum nickel concentrations in the low-to-mid mg/l range, and consistently reported many values in the 100-900 µg/l range.

6.3 SUMMARY

The range of concentration levels at which nickel has been found to cause chronic and acute toxic effects to aquatic biota is quite broad, less than 1 mg/l to greater than 1000 mg/l. Water quality considerations, $CaCO_3$ content in particular, and the chemical form of nickel present have a significant effect on the toxicity levels observed. In general, however, the threshold of toxic effects to most fish and invertebrates is in the range of 1-10 mg/l.

Concentrations at or above this range are of concern to aquatic systems. The STORET data base for the 10-year period 1970-1979 reported approximately 50 observations of nickel levels greater than 1 mg/l in the entire United States. These were distributed over several river basins and not concentrated in any one area. In addition, there were several observations of nickel in the range of 100-500 µg/l, levels which have been found to cause chronic effects to algae and freshwater fish eggs. Although the Ohio River Basin reported maximum levels in the 100-900 µg/l range over the 10-year period, the number of these observations was not frequent enough to be of concern. Overall in the United States the levels of nickel reported in streams is below 100 µg/l, so that aquatic biota would not be considered to be exposed to harmful concentrations of nickel.

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7.0 RISK CONSIDERATIONS

This chapter evaluates the human and non-human risk associated with exposure to nickel based on available data on effects and known exposure levels in the environment that were documented in chapters 5.0 and 6.0.

7.1 HUMAN RISK

The risk of adverse human effects due to exposure to background levels of nickel through ingestion, inhalation, and percutaneous exposure has not been found to be particularly great. Certain nickel compounds, however, are potentially toxic at elevated doses and/or as a result of routes of exposure which enable the compounds to accumulate at high concentrations at the cellular or subcellular levels of the body. An important factor in considering the risk of nickel toxicity is adequate assessment of whether or not nickel can reach the susceptible sites in the organism. Ingested nickel is believed to have low toxicity because it is poorly absorbed. As a result high levels of nickel in the diet of experimental animals are tolerated with minimal effects.

The major area of concern is nickel exposure through inhalation which has been shown, in certain circumstances, to cause toxicity. Exposure to nickel through inhalation is probably most prevalent in the industrial occupational setting. The animal studies evaluated in Chapter 5.0 indicate that nickel carbonyl and nickel subsulfide are carcinogenic. Other adverse effects identified in the animal studies were:

- nickel carbonyl was teratogenic and fetotoxic and
- high levels of nickel in drinking water or diet had adverse effects in neonates.

Finally, an observed human effect reported in the literature indicated that nickel contact dermatitis occurs but is not fatal.

Considering these human effects and identifiable routes of exposure, human risk is addressed in the context of four exposure scenarios: ingestion of drinking water, inhalation of ambient air, inhalation of cigarette smoke, and percutaneous exposure. In addition a brief review of occupational exposure data was made.

7.1.1 Ingestion of Drinking Water

The lowest dosage of nickel found in animal studies to cause adverse effects was 443 μg Ni/kg body weight/day. Nickel is found in drinking waters and in foods of the average diet. Drinking waters typically contained nickel at around 10 μg/l, although concentrations were occasionally higher (50 μg/l to 75 μg/l). At these levels and considering an average daily water consumption of 2 liters, drinking water is a minor constituent (less than 15%) of the average dietary intake of nickel--100 μg to 900 μg. This dietary intake corresponds to a daily dose of 1.4 to 12.9 μg nickel/kg body weight/day, which is far below the adverse effects level of 443 μg nickl/kg body weight/day.

Neither nickel in drinking water nor that contained in dietary foods can be considered a human health risk due to the low levels found in the environment and the fact that nickel is poorly absorbed or rapidly excreted from the body.

7.1.2 Inhalation of Ambient Air

The primary route of exposure to nickel which has been shown to cause adverse health effects is the inhalation route. In the animal studies the most common effects of exposure to nickel carbonyl and nickel subsulfide were the occurrence of respiratory tract cancers and neoplasms of the lung.

Considering an exposure scenario in which humans inhale ambient air, levels of "nickel" in the air and the associated speciation of nickel must be identified. In ambient air, it is unlikely that nickel carbonyl ($Ni(CO)_4$) will persist for any significant length of time due to the unstable nature of $Ni(CO)_4$. It is more probable that in the case of ambient air exposure, nickel subsulfide (Ni_3S_2) will occur as the compound causing adverse effects; by its physical-chemical nature, Ni_3S_2 is more likely to persist in the atmosphere, particularly in the vicinity of combustion sources.

Concentrations of nickel in ambient air have been reported for urban, non-urban, and industrial locations. In the urban and non-urban environment, "nickel" concentrations are low (0.6 to 690 $\mu g/m^3$); if all of the reported "nickel" were nickel subsulfide, risks associated with this exposure could be evaluated. However, speciation of the reported nickel concentrations in air has not been reported, consequently a statement of risk cannot be made. Sampling of industralized urban areas would provide more reliable data on actual concentrations in the air and associated nickel speciation. Such information would allow for a more complete evaluation of risk of exposure to ambient air.

7.1.3 Inhalation of Cigarette Smoke

Stahly (1973) reported that cigarette smoke may contain 3 μg nickel carbonyl per liter of smoke. The smoking conditions were 36-ml puffs and approximately 14 puffs per cigarette, or ~500 ml of smoke per cigarette, which contains about 1.5 μg of nickel carbonyl. These measurements are somewhat theoretical and need to be confirmed. Moreover, the respiratory retention of nickel carbonyl during smoking is not known. If one assumes these measurements are accurate and if retention is taken to be about 66%, then each cigarette contributes about 1 μg nickel carbonyl in absorbed dose. From Table 5-10, an equivalent one-pack-a-day lifetime smoker

($\sim$ 2 packs/day for 35 years) is predicted to be at an excess lifetime per capita risk of 0.05 to 0.1% due to the nickel carbonyl alone.

According to the Surgeon General's report (U.S. DHEW 1979), lung cancer is the number one cause of death due to malignancy, and cigarette smokers are at up to 20 times the risk of non-smokers of dying of lung cancer. It is estimated that there are 390,000 deaths from all cancer in the United States yearly, including 92,400 from lung cancer. In 1976, the estimated age-adjusted mortality rate due to lung cancer was 63/100,000/year for males and about 19/100,000/year for females.

The actual contribution of nickel carbonyl in cigarette smoke to the incidence of lung cancer and cancers at other sites in the body can not readily be estimated; however, the prediction from Table 5-10 is not totally unrealistic. For example, the lifetime probability of death due to cancer from the above data is estimated to be about 13% ($390{,}000 \times 70/215 \times 10^6$) and of cancer of the lung, about 3%. Of the 13% or 3%, the predicted contribution from an equivalent lifetime one-pack-a-day smoking habit (0.05-0.1%) is a small fraction.

7.1.4 Inhalation in the Occupational Environment

Occupational exposure to nickel compounds via inhalation was considered in this risk assessment primarily as a means to put waterborne and dietary exposure in perspective. Occupational exposure to nickel carbonyl and nickel subsulfide is most likely to occur in the ferrous metals (iron and steel), electroplating, and nickel refining industries. It is in these environments that nickel carbonyl and subsulfide are both likely to occur, and likely to persist long enough to allow exposure at levels sufficient to cause adverse human effects. A cursory review of occupational exposure data indicated that data on speciation of nickel were not available: all nickel reported in occupational data was in the "general" form. Consequently, it was not possible to evaluate exposure to or risk associated with these compounds in the occupational environment, although it is probable that exposure occurs. Neither compound is found in the aquatic environment or in food, thus there is no exposure via ingestion of drinking water or in the diet.

7.1.5 Nickel Contact Dermatitis

A number of studies summarized in the NAS report (1975) indicate that patients with dermatitis frequently react to nickel patch tests (between 6 and 15%). Unanswered, however, is the incidence of nickel sensitivity in the general population, and, more importantly, what is the capacity of nickel, in the variety of ways that the general population is exposed, to act as a skin sensitizer.

The most frequently reported causes of nickel allergy are from jewelry (especially earrings) and clothing fasteners. Typically, women have a much higher incidence of nickel sensitivity than men. Interestingly, so-called "hypoallergenic" posts for pierced earrings, manufactured for people who apparently have developed allergies to the 14-karat gold posts, contain nickel. The ability of stainless steel kitchen appliances and cookware to sensitize persons to nickel is unknown.

7.1.6 Conclusions

The risk associated with exposure to nickel is primarily confined to inhalation of cigarette smoke and possibly ambient air if most of "nickel" in ambient air is in the form of nickel subsulfide. The risk associated with inhalation of nickel carbonyl in cigarette smoke is only a small fraction of the risk associated with the other components of cigarette smoke; in the case of nickel carbonyl an excess lifetime per-capita risk is estimated at 0.05 to 0.1%. The risk of exposure to nickel subsulfide in ambient air cannot be evaluated until further sampling and analysis of nickel speciation is performed in the industrial and urban environments. Similarly risk associated with exposure to nickel carbonyl or subsulfide in the occupational environment cannot be evaluated without further data. Dermatitis caused by contact with nickel-bearing objects is not fully understood but is not considered a life-threatening problem. There is no identifiable risk associated with ingestion of nickel in drinking water and the diet.

7.2 NON-HUMAN RISK

Nickel is occasionally found in surface freshwaters at concentrations (total) exceeding the lowest effects levels (dissolved) reported for aquatic organisms. Additionally, the criteria to protect freshwater aquatic life at a 24-hour average and maximum concentration (set for soft waters) are violated or almost exceeded by maximum surface water concentrations on numerous occasions, most notably in the soft waters of the North Atlantic major river basin. Under certain circumstances, nickel occurs in concentrations in surface waters at levels sufficiently high to potentially cause adverse effects in aquatic species, based on information developed under laboratory conditions. Little field data regarding nickel toxicity in natural systems are available to confirm this hypothesis. Mean surface water concentrations rarely exceed these criteria.

7.2.1 Exposure

In order to ascertain the potential risk of aquatic organisms in relation to nickel, it is necessary to compare effects levels to exposure levels. In the case of nickel, as for other metals, this is difficult because adverse effects levels are determined for dissolved nickel salts and exposure concentrations report total nickel. Nickel is highly soluble at neutral pH in soft waters; however, nickel in water is commonly associated with suspended solids and sediment, reducing its biological availability. Only a fraction of the nickel concentration typically reported in monitoring data is biologically available, making the "actual" concentration (in terms of availability) lower than the reported level. This increases the gap between effects and exposure levels. Unfortunately, determining this fraction on a national scale is not possible due to its dependence on pH, hardness, concentrations of suspended solids and complexing agents, and other factors some of which vary independently. A site-specific analysis is required for this type of interpretation of total nickel concentrations.

As a worst case assumption, all of the nickel reported in total concentration measurements can be considered available. As discussed in Chapter 6.0, typical surface water concentrations over the past 10 years were below 0.5 mg/l. In 1970 the mean concentrations in 16 river basins ranged from 0.003-0.03 mg/l. On occasion, concentrations were reported between 0.5-50 mg/l. The maximum reported concentration was 800 mg/l.

7.2.2 Aquatic Effects and Risk Considerations

Chronic effects levels are commonly reported for fish living in soft freshwater at greater than 2 mg/l. Invertebrates are more sensitive, with the lowest observed effects level at 0.5 mg/l. Saltwater species, according to the limited data available, are less sensitive than freshwater species. These effects are discussed more fully in Chapter 6.0.

Table 7-1 presents the effects and exposure concentrations for comparison. Nickel concentrations in surface water are typically below effects concentrations; this is also true for most sensitive species. Only certain algae species may be affected at typical ranges of nickel concentration. However, the high exposure concentration range, such as is associated with rare observations in the Ohio River Basin most recently (1978, 1979) and others in the past, is equivalent to the concentration range causing acute effects in most freshwater species. Assuming total availability on these occasions of high nickel concentrations, aquatic species are at risk of deleterious effects in certain river basins for short periods of time. However, as discussed previously, the assumption of total availability is an unreasonable one. To better define the risk, a metal speciation model using local system parameters (e.g. pH, etc.) must be implemented to calculate available nickel concentrations. Salt water concentrations were not available so it was not possible to evaluate the risk of marine populations in regard to nickel.

7.2.3 Sensitive Species

The aquatic species reported to be most sensitive to nickel concentrations in water according to the available data are listed in Table 7-2. It is interesting to note, however, that the range of effects levels for most freshwater species is a narrow one of approximately one order of magnitude. Therefore, the difference between the levels at which adverse effects are experienced by the most sensitive species and those experienced by other species is not very extreme.

7.2.4 Regional Areas of Higher Risk

The major river basins in which a number of nickel concentrations were higher than the mean included the North Atlantic, Tennessee, Ohio, Missouri, S. Central Lower Mississippi, Lake Erie, and Lake Michigan. The highest reported nickel level was in the North Atlantic. These observations were infrequent and, therefore, are not believed to be typical nickel concentrations for these major river basins.

TABLE 7-1. COMPARISON OF REPORTED EFFECTS AND EXPOSURE LEVELS FOR AQUATIC ORGANISMS

EXPOSURE LEVELS	Typical	High	Maximum
Fresh Surface Water[a]	0.001-0.5	1.0-50	800
Salt Water (background concentration)	0.0054	No monitoring data available for concentrations resulting from anthropogenic sources.	

	Soft Water (<100 mg/l as $CaCO_3$)		Hard Water (>100 mg/l as $CaCO_3$)
EFFECTS LEVELS[b]	Most Species	Most Sensitive Species	Most Sensitive Species[c]
Freshwater Fish	10-50	0.8[d]	27
Freshwater Invertebrates	1-30	0.5	3.8
Salt Water Fish[e]	14-350	14.6	-
Salt Water Invertebrates	20-300	13.9[f]	-
Freshwater Algae	-	0.1	-

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[a] Data from STORET Water Quality System retrieved on July 22, 1980; discussed in Chapter 6.0 in which total nickel concentrations given.

[b] Applies to acute and chronic effects; dissolved nickel concentrations given.

[c] Not enough data were available to differentiate between sensitive and typical species.

[d] For Stickleback, in estuarine species, in nickel nitrate.

[e] Concentration does not consider water hardness.

[f] For nickel sulfate.

TABLE 7-2. SPECIES SENSITIVE TO NICKEL CONCENTRATIONS IN WATER[a]

Freshwater Fish	Fathead minnow (Pimphales promelas), goldfish (Carassius auratus), guppy (Lebistes reticulatus) and bluegill (Lepomis macrochirus).
Estuarine Fish	Stickleback
Marine Fish	Atlantic silversides
Freshwater Invertebrates	Daphia (Daphia magna, D. pulicaria and D. hyalina) and rotifer (Philodina acuticornus)
Salt Water Invertebrates	Sandworm (Nereis virens) and Hermit crab (Pagurus longicarpus)
Algae	Scenedesmus acuminata

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[a] All data discussed in Chapter 6.0.

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APPENDIX A

NOTE 1: Hanna mines garnierite $(Ni \cdot Mg)_6Si_4O_{10}(OH)_8$ and several associated minerals which occur in altered periodotite. The ore, which averages 1.2% nickel, is removed with power shovels and trucks; blasting is not a common practice (Matthews, 1979). The ore is screened at the mine and either sent directly to the tramway surge pile or to the crusher and all boulders are rejected. Efforts to blend the ore into a uniform feed for the melting furnaces begin at the mine and continue throughout all subsequent operations.

Once the ore is crushed, the material is visually classified (the intensity of the green color of garnierite is directly proportional to the nickel content [Boldt, 1967]) and directed to the ore product or reject stockpile. From the product stockpile, the materials are calcined and preheated either in a rotary kiln or a multihearth furnace. The ore is next melted in either an electric or a melting furnace and poured into reaction ladles where reduction by addition of crushed ferrosilicon occurs. Coke, lime, and iron ore are also added to produce the end product--ferronickel.

NOTE 2: The first settling pond received about 12,500 liters of process water per minute ($l\text{-min.}^{-1}$) of which 9,800 $l\text{-min}^{-1}$ were returned to the process. Approximately 1,500 $l\text{-min}^{-1}$ were lost by evapotranspiration and underflow to a nearby creek. Thus, overflow to the second pond amounted to nearly 1,200 $l\text{-min}^{-1}$. The second pond also received mine site runoff water whose volume ranged widely throughout the year, (i.e., zero for approximately six months and as high as 2.2 million liters per day during the rainy season). Though the second pond had no surface discharge during the dry season, inputs balanced by evaporation and an undermined subsurface flow to a nearby creek, significant discharges did occur during the rainy season. Average discharge over the year amounted to 455,000 liters per day with a mean nickel concentration of 0.03 mg/l. Therefore, approximately 5 kilograms of nickel were discharged from the second holding pond based on a year-round operation. (The concentration of nickel in the wastewaters was determined by analyses of samples collected from the second settling pond and was comparable to values obtained by company personnel (0.038 mg Ni/l of wastewater).

NOTE 3: Production at AMAX Nickel Refinery was impaired during the last four months of 1979 by a work stoppage (Sibley, 1980).

NOTE 4: Based on 1980 nationwide particulate emissions from steel manufacture, and assuming similar quantities of particulates were emitted in 1979, and 750 ppm nickel (or 750 g Ni/kkg particulates):

Furnace Types	Particulate Quantity (kkg)	Nickel Emitted (kkg)
Open Hearth Furnace	27,573	21
Basic Oxygen Furnace	19,501	15
Electric Arc Furnace	21,768	16
	Total	52 kkg

NOTE 5: Based on production figures from Sibley (1980) and wastewater discharge data from secondary copper smelters/refiners (EPA, 1979a; Table 3.4), it is known that: total amount of copper-base scrap processed in 1979 = 3,240 kkg (100%); amount of that total from new scrap = 2,800 kkg (or 86%); amount from old scrap = 440 kkg (or 14%), then 86% and 14% of total waste stemmed from processing of new and old copper-base scrap, respectively.

A total of 565 kkg and 92 kkg of nickel wastes were generated from refining of new and old copper-base scrap, respectively. Of the 32 known secondary copper smelter/refiners, 20 have no discharge; 7 are direct dischargers, 5 are indirect dischargers (EPA, 1979a). Assuming that the total discharge is divided equally among the remaining 12 plants, then 327 metric tons and 237 kkg of nickel were discharged to surface and POTW sinks, respectively from plants processing new copper-base scrap. Likewise 53 kkg and 38 kkg of nickel were discharged to surface and POTW sinks, respectively by plants processing old copper-base scrap.

NOTE 6: Less than 1 kkg of nickel is assumed to be produced based on the following data: (1) Few plants practice coproduct nickel recovery; (2) those that do recover coproduct nickel have efficient systems because the most widely used evaporators are closed systems so that aerosols are recycled; (3) discharges from centrifuges are recycled to electrolytic cells; and (4) slimes are processed for metal recovery (see Figure C.3, Appendix C; EPA, 1975c; and Outokumpu Engineering Inc., 1980).

NOTE 7: Negligible is defined here as <1 kkg; 754,082,000 kkg of distillate fuel were consumed in 1979 in the U.S.; one liter of distillate fuel weighs approximately 845g or 0.000845 kkg (EPA, 1977a), therefore 8.9×10^{11} liters of distillate fuel were consumed for that year. If the average nickel concentration of 4.75 μg/ml determined from 17 distillate fuel oil number 2 samples (Lee and Duffield, 1979) represents a typical nickel concentration for distillate fuels, then approximately 4 kkg of nickel were contained within all the distillate fuel consumed. Taking into account control device efficiencies, the quantity of nickel emitted to the atmosphere would most likely be <1 kkg.

Low concentrations of nickel have been reported to be associated with automobile exhausts. This nickel most likely results from ablation rather than combustion of fuel because: (1) very small quantities of nickel have been identified in fuels, (2) the exhausts tested came from automobiles equipped with nickel-containing reduction catalysts and (3) the rate of nickel emission decreased rapidly with mileage accumulation (Lee and Duffield, 1979).

NOTE 8: Based on Hamilton Standard electroplating data base, of the total 443 electroplating facilities whose effluents contained nickel, the average flow rate = 22,700 liters per hour and the average nickel concentration = 3.4 mg/l. Based on a 365 day/yr operation and 16 hr/day, then 0.45 kkg/yr/plant was discharged. Nearly 75% of electroplating facilities discharged to POTWs; the remaining 25% discharged to rivers or basins. Given that 200 kkg nickel discharged as effluent represented 5% of the total wasteload, approximately 3,800 kkg of nickel were disposed of in sludge annually (based on average nickel removal efficiencies of 95% at electroplating facilities, Patterson, 1976; Masarik, 1980). Approximately 80% of electroplaters release sludges to public or private landfills; the remainder is claimed off site. Thus, 3,040 kkg of nickel were disposed to land in 1979.

NOTE 9: In 1977 more nickel sulfate was produced than any other nickel compound. Assuming 1979 production figures to be comparable to 1977 values and based on the manufacturing process (i.e., filtration sludges were reprocessed and treatment tank liquors recycled, EPA 1977b), engineering judgments indicate that approximately 3 kkg of nickel were released to land and water, each. Nickel concentrations in wastewater sludges from woven fabric and dying facilities averaged 32 mg/l. Assuming wet sludge to be 95% water by weight and the total sludge output to be 28,000 kkg/yr, then 1 kkg of nickel contained in sludge was disposed to land.

NOTE 10: Based on EPA estimates (1975a and 1976), approximately 1,470 kkg of nickel were used in battery manufacture in 1979. Based on EPA questionnaire surveys (1973b), 4 kg of nickel were emitted to the atmosphere per kkg of nickel processed. Of the 10 battery facilities, 8 were direct and 2 were indirect dischargers. Based on EPA effluent discharge rates (after treatment), 15 kg Ni/kkg batteries produced and a total production of 890 kkg by the 2 indirect dischargers, 13 kkg of nickel were sent to POTWs. The 8 remaining plants discharged 0.01 kg Ni/kkg batteries produced (production of 3,560 kkg batteries), therefore less than 1 kkg was discharged to waterways directly.

Based on 1.7 kg Ni in sludge from wastewater treatment at the 2 indirect plants/kkg batteries produced, and a total production of 890 kkg batteries. Therefore 2 kkg of Ni were discharged to land as sludge. Two of 10 plants disposed of scrap cells to land. Based on an EPA discharge rate of 1.5 kg Ni/kkg batteries produced and a total production of 890 metric tons, 1 kkg of Ni was disposed to land as scrap.

NOTE 11: The nickel content of sea water ranges from 0.1-0.5 $\mu g/l$ (NAS, 1975). Therefore, with an enrichment factor of 200 and a total aerosol production from sea salt sprays of 10^6 kkg annually (Nriagu, 1979), approximately 40 kkg of nickel were aerosolized from this source in 1979.

NOTE 12: Nriagu (1979) estimated world-wide nickel emission from volcanic activity to range from 2,400 to 56,000 kkg annually with a value of 3,800 kkg being most likely.

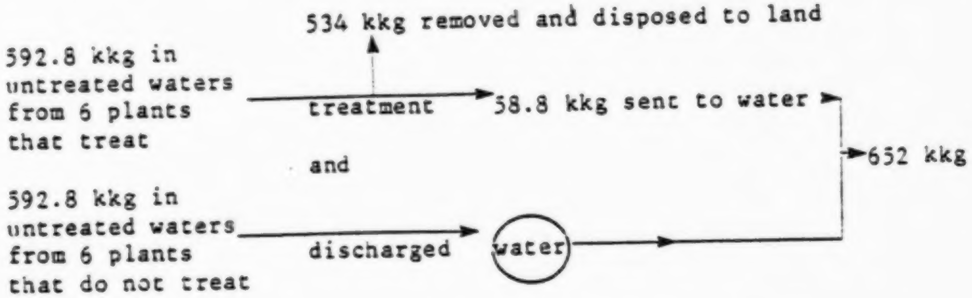
NOTE 13: Aerosol formation from forest fires has recently been discussed by Young and Jan (1977) who measured dry deposition rates of nickel in the area covered by a forest fire smoke plume. Nickel deposition fluxes ranged from 0.01 to 0.13 $\mu g/m^2$/day and averaged about 0.07 $\mu g/m^2$/day during the fire; postfire values of nickel deposition flux is approximately 0.01 $\mu g/m^2$/day. Based on these data, aerial nickel fallout to a 10,000 km^2 area was estimated to be 120 kg/day and 33 kg/day from fire and nonfire sources, respectively. Aerosol nickel is removed eventually from the atmosphere by dry deposition and/or washout, although the rates of removal are unavailable.

NOTE 14: Significant amounts of nickel may be released to the atmosphere from vegetation. The most likely manner in which plants exudate nickel is that nickel associated with particles of various sizes is released from the plant surfaces during rapid growth and/or transpiration. It is possible that epicuticular waxes are the nickel carriers and that fragmentation and loss of wax rodlets occur during rapid leaf expansion. Alternatively, there may be a mechanism which involves the production of airborne salt crystals generated by diffusiophoresis associated with water loss during rapid transpiration. Assuming vegetation exudates to approximate 75 x 10^6 kkg annually, an average ash content of 11%, and nickel concentration in ash residue to be 25 g/g then 200 kkg were emitted from this source. (Goldsmith and May, 1966; Beauford and Barber, 1977.)

NOTE 15: Nickel, as referred to here, means nickel contained within an alloy; generally $\leq$50%.

NOTE 16: Old nickel-based scrap contains varying percentages of nickel (and impurities) and is processed at many different plants whose recovery efficiencies and disposal practices vary. Also, the flow of this scrap is difficult to follow due to the number of different groups who handle secondary scrap (see Figure C-4, Appendix C).

NOTE 17: The annual unit flow rate of water from waste electrolyte (electrolytic refining area cleaning water) was 31.9 x 10^6 l/yr. The nickel concentrations in treated and untreated wastewaters were 310,000 and 3,100,000 μg/l, respectively; therefore 9.8 and 98.8 kkg of nickel were contained in the total volume of treated and untreated waters from one plant, respectively. Six secondary copper refineries practiced treatment and six did not. Therefore, 6(9.8 kkg) + 6(98.8 kkg) of nickel, or (58.8 kkg) + (592.8 kkg) = 651.6 kkg was released to water. Furthermore, 6(98.8 - 9.8) = 534 kkg of nickel were removed during treatment and disposed to land, i.e.:


534 kkg removed and disposed to land
592.8 kkg in untreated waters from 6 plants that treat
treatment
58.8 kkg sent to water
and
652 kkg
592.8 kkg in untreated waters from 6 plants that do not treat
discharged
water

NOTE 18: Miscellaneous industries include: cement manufacturing, asbestos production, primary and secondary ferrous and nonferrous smelting/refining, food processing, textile and fur industries, laundries, and car washes.

NOTE 19: Stationary sources include: power generating plants and steam generating plants for industrial, business and residential use. Mobile sources include trucks and automobiles.

NOTE 20: Nickel is known to preferentially concentrate in respirable particles (Natusch, et al., 1974). The smaller the particle (particularly those $<1\ \mu$m) the greater the likelihood that they deposit predominantly in the alveolar regions of the lungs where the absorption efficiency for most trace elements is 50 to 80 percent. Therefore, the smaller flyash particles (i.e., $<3\ \mu$m) which bypass the control devices into the atmosphere pose the greatest potential health hazard (Lee and Duffield, 1979).

NOTE 21: Fuel oils are broadly classified into two major types: distillate and residual. Distillate oils (fuel oil grades 1, 2, and 4) are used mainly for residential and commercial applications where easy fuel burning is required. Distillate fuels not only are more volatile and less viscous than residual oils (which require preheating to be pumped) but also are cleaner and contain negligible ash (see Appendix B, Note 7). Residual oils (fuel oil grades 5 and 6) are used mainly in utility, industrial, and large commercial applications. Because residual oils are produced from the residue after the lighter fractions (i.e., gasoline, kerosene, and distillate oils) have been distilled from crude oil, significant quantities of ash are often present.

NOTE 22: Flue gas cleaning equipment is generally employed only on large oil-fired boilers. Mechanical collectors are primarily useful in controlling particulates generated during soot blowing, upset conditions, or when a very dirty, heavy oil is fired. During these situations, high efficiency cyclonic collectors can control up to 85 percent of the particulates, but when a clean oil is combusted, they will not be as effective. Electrostatic precipitators are commonly found in power plants that at one time fired coal. Precipitators that were designed for coal flyash provide only 40 to 60 percent control of oil-fired particulate, while 90 percent collection efficiencies have been reported for new or rebuilt devices specifically designed for oil-firing units. Scrubbing systems have been installed on oil-fired boilers, to control particulate. These systems can achieve particulate control efficiencies of 50 to 60 percent (EPA, 1977a).

NOTE 23: The major asbestos mineral used commercially, chrysotile ($Mg_6(OH)_8Si_4O_{10}$), generally contains 1.5-1.8 mg nickel/g of chrysotile as an isomorphic substitution for magnesium (Streib, 1978). Dusts from milling of asbestos could release small quantities of nickel, as a component of chrysotile, to the atmosphere; moreover tailings from milling operations are dry piled, providing a possible route for nickel discharge to either the atmosphere via wind erosion or aquatic environments via leaching.

According to EPA plant trip data, an asbestos mill producing 36,300 kkg/year and using a baghouse collection system emits 0.18 kkg asbestos/yr (Wood, 1980). Assuming this emission rate to be similar for all of the five U.S. asbestos mills which produced 93,300 metric tons asbestos in 1979 (Clifton, 1980) with a maximum nickel content of 1.8 mg/g in chrysotile, less than 1 kkg of nickel was directly emitted to the atmosphere.

Possibly a more significant source of nickel release to the environment from asbestos production is the dry piling of waste tailings. Because recovery of asbestos fiber from ore is low (i.e., 5% to 50%), a significant amount of chrysolite remains in the waste (Streib, 1978). Further, because chrysolite reacts with acids, weathering of waste tailings may release significant amounts of nickel to the environment. The magnitude of this source, however, is unknown.

NOTE 24: Other methods of electroplating wastewater treatment are reverse osmosis, evaporation, ion exchange, and electrodialysis.

NOTE 25: Nickel azo yellow (Colour Index number 12775), a 2:1 nickel complex of a bidentate o-hydroxyazo ligand, is used for its green-yellow color in PVC and other vinyl plastics, particularly where light stability is important (e.g., automobile parts). Nickel antimony titanate is formed by high temperature fusion (< 1000°C) of nickel antimonate and titanium oxide in dry form. The pigment is extremely insoluble as the nickel antimonate takes position in the titanium oxide lattice structure. Though the amount of pigment contained per liter of paint depends on the particular color, yellow paint averages 22-360 g/l. Nickel dimethylglyoxime, a red pigment, is not commercially produced in significant quantities.

NOTE 26: Hydrotreating is an oil refining process using a cobalt-molybdenum catalyst to reduce the sulfur and nitrogen content of crude oil (Miller, 1979). Smaller amounts of nickel-molybdenum catalysts are used for hydrotreating as well. Cobalt is in short supply however, and increased use of nickel-containing catalysts is being encouraged. Nickel catalysts are superior to cobalt catalysts in terms of nitrogen removal, but do require higher operating pressures.

NOTE 27: A framework for calculating the total nickel flow through the nation's POTWs (see Table C-17 in Appendix C) is provided by data from a recent EPA study. A material balance of nickel at the treatment plants can be constructed using a total POTW flow of approximately 10^{11} l/day (EPA, 1978c) and median values of 180 g Ni/l (influent) and 107 g Ni/l (effluent). It is assumed for purposes of these calculations that influent and effluent flow rates are equal, i.e., that water loss from sludge removal and evaporation is small compared to influent flows. It is further assumed that while nickel is recycled within the activated sludge process, all will eventually be wasted. Thus, the value for nickel in sludge is simply the difference between the influent and effluent nickel totals, as there is an assumed negligible loss of nickel to the air. Using the assumptions, 2,660 kkg of nickel were disposed as sludge to land from POTWs in 1979 and approximately 3,900 kkg of nickel were discharged to water from POTW effluent streams. An alternative method for estimating the annual nickel release to sludge is as follows: the quantity of dry sludge produced in 1979 was 6 x 10^6 kkg; assuming the nickel concentration of POTW wet sludge to be 8 mg/l where wet sludge is 95% water by weight, approximately 960 kkg would have been discharged to land (EPA, 1979d). Approximately 25% of all municipal sludge is landfilled, 25% spread on land, 15% ocean dumped, and 35% incinerated (EPA, 1979c).

NOTE 28: Based on soil studies, nickel solubility (like most other heavy metals) increases with soil pH. Within the pH range of 4-8, organic matter in soils forms nickel complexes which effectively preclude further migration or plant uptake (Antonsen and Springer, 1968).

APPENDIX B

This distribution of nickel emissions and discharges from combustion of coal and oil* for energy production is derived from the following basic assumptions.

(1) The ash present in coal is distributed between bottom ash, flyash collected, and particulate stack emissions (i.e., ash loss via slagging is negligible); and

(2) the distribution of the nickel originally present in the feed material is dependent only upon particle size.

Thus: Ash in (A_{in}) = Ash out (A_{out}) $= A_b + A_c + A_e$, or

$$1 = A_{in} = A_b + A_c + A_e$$

where A_b = Fraction Bottom ash

A_c = Fraction Flyash collected

A_e = Fraction Flyash emitted, also,

$A_c + A_e = A_f$ where A_f = Fraction of ash that is total flyash.

The amount of ash which appears as bottom ash, is dependent upon fuel and boiler type. For boilers which fire pulverized coal (≤ 1 cm) eighty percent of the ash originally present in coal is estimated to appear as flyash; ash produced in cyclone boilers, which burn a somewhat larger size of coal than pulverized coal fired units, is distributed about equally between bottom ash and flyash; of the ash produced in stoker fired boilers, which burn relatively large sizes of coal (≥ 10 cm), approximately twenty-five percent appears as flyash.

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*Though the derivation is applicable to gas fired boilers as well, natural gas contains negligible amounts of nickel and thus is an insignificant source of nickel emissions to the environment (Slater and Hall, 1977).

Essentially all of the ash present in residual oil appears as flyash. The amount of flyash collected in turn depends upon the particulate control device used, (either singlely or in combination), which generally are cyclonic devices, electrostatic precipitators and baghouses. The fraction of ash emitted as flyash, control device efficiency, application of control, effective efficiency, fine particulate fraction, atmospheric emission fraction, and land dispersion fraction are shown in Table B-1. For pulverized coal-fired boilers, ash emission fractions are calculated as follows:

$$(1-A_f) = A_b = 0.20$$

$$A_c = (A_f)E = 0.71$$

$$A_e = (A_f)(1-E) = 0.088$$

The fraction of the ash emitted to the atmosphere (A_e) is further subdivided into particulate which remains suspended (A_e <3 μm) and that which eventually settles to land (A_e >3 μm) in the following way:

$$A_e > 3\mu = A_e P_f = 0.057$$

$$A_e < 3\mu = A_e(1-P_f) = 0.031$$

Nickel emissions and discharges within a boiler are a function of particle size, nickel concentration increasing with decreasing particle size. Nickel concentration of flyash by particle size ranges is shown in Table B-2. Using these data (and assuming the nickel concentration of bottom ash and collected flyash to be equal) relative nickel concentrations of bottom ash (C_b), collected flyash (C_c) flyash emitted > 3μ (C_e< 3μ), and flyash emitted <3μ (C_e>3μ) are calculated to be 1.0, 1.0, 3.9, 10.5, respectively. Nickel emission factors are calculated in the following way.

$$1 = f_b + f_c + f_{e<3\mu m} + f_{e>3\mu m}$$

where

f_b = Fraction of nickel contained in bottom ash

f_c = Fraction of nickel contained in collected flyash

$f_e<3\mu$ = Fraction of nickel emitted as particulate $<3\mu$

$f_e>3\mu$ = Fraction of nickel emitted as particulate matter $>3\mu$.

These fractions are calculated using ash emission fractions and relative nickel concentrations:

$$Ni_{total} = A_b \cdot C_b + A_c \cdot C_c + (A_{e<3\mu} \cdot C_{e<3\mu}) + (A_{e>3\mu} \cdot C_{e>3\mu})$$

$$f_b = \frac{A_b \cdot C_b}{Ni_{total}}$$

$$f_c = \frac{A_c \cdot C_c}{Ni_{total}}$$

$$f_e<3\mu m = \frac{A_{e<3\mu m}\ (C_{e<3\mu m})}{Ni_{total}}$$

$$f_e>3\mu m = \frac{A_{e>3\mu m}\ (C_{e>3\mu m})}{Ni_{total}}$$

Consequently, nickel emission factors by boiler type and media are shown in Table B-3.

Table B-1. Mass Efficiency of Particulate Collection on Utility Boilers[a]

Fuel	Boiler Type	Fraction of[b] Ash Emitted As Flyash (A_F)	Control Device Efficiency[c]	Application of Control[d]	Effective Efficiency		Fine Particulate Fraction (<3 µm) (P_f)	Atmospheric Emission[h]		Land Dispersion[h]	
					Calculated	Reported[f] (E)		(<3 µm) Ae <3 µm	(>3 µm) Ae >3 µm	Flyash	Bottom Ash
Coal	Pulverized	0.8	0.92	0.97	0.89	0.89	0.35	0.031	0.057	0.71	0.20
	Cyclone	0.50	0.91	0.71	0.65	0.88	0.52	0.031	0.029	0.44	0.50
	Stoker	0.25	0.80	0.87	0.70	0.65	0.14	0.012	0.075	0.16	0.75
Oil	All	1.0	0.50	0.20	0.10	0.10	0.90	0.81	0.19	-----	-----
Gas	All	1.0	0	0	0		0.90	0.90	0.10	-----	-----

a) Data were obtained from utilities accounting for one-half of the total U.S. utility consumption of coal in 1974.

b) Engineering estimates based upon published data.

c) Fraction collected of the total particulate mass entering control devices. Data includes both test results and reported design efficiencies.

d) Fraction of utility boiler equipped with particulate control devices.

e) Effective efficiency equals control device efficiency multiplied by application of control.

f) Slater and Hall, 1977.

g) Fine particulate fraction is the fraction of total particulate mass emission <3 µm, derived from particulate size distribution entering control device; the effective mass efficiency; and the effective fine particulate efficiency.

h) Fraction emitted based upon reported effective efficiency, fine particulate fraction, and distribution of coal ash between flyash and bottom ash. For pulverized and cyclone boilers, the distribution fraction between flyash and bottom ash (engineering estimates based upon unpublished data) is estimated to be 0.8 and 0.2 respectively; for stoker fired boilers, the distribution fraction between flyash and bottom ash is estimated to be 0.2 and 0.8 respectively.

Source: Slater and Hall, 1977.

Table B-2. Nickel Concentration in Coal Flyash as a Function of Particle Size

Particle Diameter (μm)	Nickel Concentration μg/g	Mass Fraction (%)
Flyash retained in the plant		
Sieved fraction:		
>74	100	66.30
44-74	140	22.89
Aerodynamically sized fractions		
>40	300	2.50
30-40	130	3.54
20-30	160	3.25
15-20	200	0.80
10-15	210	0.31
5-10	230	0.33
<5	260	0.08
Airborne flyash[a]		
>11.3	460	
7.3-11.3	400	
4.7-7.3	440	
3.3-4.7	540	
2.1-3.3	900	
1.1-2.1	1600	

Source: Natusch, et al., 1974.

[a] An equal mass distribution among particular size fractions is assumed.

Table B-3. Nickel Emission Factors by Boiler Type and Media

Fuel	Boiler Type	Nickel Distribution[a]			
		Bottom Ash (f_b)	Flyash Captured (f_c)	Flyash Emitted (<3μm) ($f_{e<3\ \mu m}$)	Flyash Emitted (>3μm) ($f_{e>3\ \mu m}$)
Coal	Pulverized	0.4	0.49	0.22	0.15
	Cyclone	0.36	0.32	0.24	0.08
	Stoker	0.56	0.12	0.10	0.22
Oil	All	----	----	0.96	0.04

[a] Fraction emitted based upon ash distribution and relative nickel concentration of flyash <3μ, flyash >3μ, flyash collected, and bottom ash. The concentration ratios are (see Table A-3 also):

flyash emitted (<3μ) = 10.5
flyash emitted (>3μ) = 3.9
flyash collected = 1.0
bottom ash = 1.0

APPENDIX C

Table C-1. Physical Properties of Nickel

Atomic number	28
Electronic configuration	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
Atomic weight	58.71
Melting point °C	1453
Specific gravity at 20°C	8.908
Crystal structure	face-centered cubic
Lattice constant at 24.8°C,A	3.5168
Thermal expansion coefficient at 0-100°C, per °C	13.3x10
Specific heat at 200°C, cal/g	0.1225
Latent heat of fusion, cal/g	73.8
Thermal conductivity, cal/(sec)(cm) (C°/cm) @ 100°C	0.198
300°C (99.94% purity)	0.152
500°C	0.148
Electrical resistivity at 20°C ohn-cm	6.844
Magnetic transformation temperature, °C	357
Boiling point, °C (by extrapolation of vapor pressure data	2730
Reflectivity, %	
@ 0.30 (ultraviolet)	41
@ 0.55 (yellow-green)	64
@ 3.0 (infrared)	87

Source: After Nicholls, 1973 and Adamec and Kihloren, 1968.

Table C-2. Solubility Products of Various Nickel Salts

Salts	μ=0[a]	μ=0.1(unless otherwise noted
$Ni(OH)_2$ (fresh)	14.7	14.3
(aged)	17.2	16.8
$Ni_2[Fe(CN)_6]$		14.9[b]
$NiCO_3$		8.2[b]
$Ni_3(AsO_4)_2$		25.5[b]
NiS_α	18.5	
NiS_β	24.0	
NiS_γ	25.7	

Source: Ringbom, 1963.

[a] Most values refer to a temperature of 20 or 25°C

[b] Ionic strength varied and was not specified.

Table C-3. Nickel-Containing Minerals

Mineral	Formula	Nickel Content, %
Silicate and Oxide		
garnierite[a]	$(Ni,Mg)_6Si_4O_{10}(OH)_8$	up to 47.0
nickel ferrous limonite	$(Fe,Ni)O(OH)\cdot nH_2O$	low but variable
Sulfides		
pentlandite	$(Ni,Fe)_9S_8$	34.22
millerite	NiS	64.67
heazlewoodite	Ni_3S_2	73.30
polydymite	Ni_3S_4	57.86
violarite	Ni_2FeS_4	38.94
siegenite	$(CO,Ni)_3S_4$	28.89
bravoite	$(Ni,Fe)S_2$	24.0
Arsenides		
niccolite	$NiAs$	43.92
maucherite	$Ni_{11}As_8$	51.85
rammelsbergite	$NiAs_2$	28.15
gersdorffite	$NiAsS$	35.42
chloanthite	$(NiAs_2)$	
Antimonide		
breithauptite	$NiSb$	32.53
Arsenate		
annabergite	$Ni_3As_2O_8\cdot 8H_2O$	29.4

[a] Garnierite is a generic term applied to a series of mixtures of hydrous nickel-magnesium silicates. Several nickel silicates, each an analog of a magnesium mineral (given in brackets) can occur as constituents of garnierite:

nimite, $(Ni,Mg,Fe,Al)_3(Si,Al)_2O_5(OH)_4$ [chlorite];
willenseite, $(Ni,Mg)_3Si_4O_{10}(OH)_4$ [talc];
pecoraite, $Ni_3Si_2O_5(OH)_4$ [clinochrysotile];
nepouite $(Ni,Mg)_3Si_2O_5(OH)_4$ [lizardite]; and
pimelite, $(Ni,Mg)_3Si_4O_{10}(OH)_2\cdot 4H_2O$ [Stevensite]

(Faust, 1966; Faust, *et al*., 1969; De Waal, 1970).

Table C-4. Nickel in Water from Major U.S. River Basins[a]

River Basin	Mean Nickel Concentration, μg/liter[b]	Frequency of Detection, %
Northwest	8	22.0
North Atlantic	8	28.1
Southeast	4	20.9
Tennessee River	4	8.8
Ohio River	31	25.2
Lake Erie	56	53.2
Upper Mississippi	15	15.2
Western Great Lakes	10	9.1
Missouri River	5	2.0
Southwest-Lower Mississippi	17	9.7
Colorado River	12	8.0
Western Gulf	3	2.1
Pacific Northwest	10	10.5
California	10	13.8
Great Basin	4	15.8
Alaska	5	11.1

Source: Koop and Kroner, 1970.

[a] The detection limit for nickel in water with total dissolved solids (TDS) of 400 μg/l was 20 μg/l; if TDS amounted to 200 μg/l, the detection limit would be 10 μg/l.

[b] Only occurrences of nickel were used in calculating the mean.

Table C-5. Relative Rates of Aerosol Production Mechanisms

MECHANISMS	RELATIVE RATE
Sea-to-Air Transport of Salts	100
Natural Gas-to-Particle Conversion	74
Wind Blown Dust	50
Anthropogenic Gas-to-Particle Conversion	38
Anthropogenic Particles	10
Volcanoes	4
Forest Fires	3
Meteoretic Debris	1

Source: Mulvey, 1979.

Table C-6. Source and Composition of Mattes Imported into the U.S., 1979[a]

Source	Average Composition (%)				
	Ni	Cu	CO	S	Fe
New Caledonian	75	0	1.5	(b)	(b)
South Africa[c] (Republic of)	40	40	0.5	16	0.2
Botswana	40	40	0.5	16.0[d]	0.2[d]
Australia[d]	75	0	1.5	(b)	(b)

Source: Hoppe, 1977, unless otherwise noted.

[a] All imported matte is processed at AMAX Nickel Division of American Metal Climax, Incorporated, Braithwaite, Louisiana.

[b] The remainder of the matte is sulphur and iron.

[c] Received in powdered form; similar in composition to the Botswana matte (Sibley, 1980),

[d] Similar in composition to the New Caledonian matte (Sibley, 1980).

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Table C-7. Nickel Wastes: Energy Production, 1979 (kkg)

Source	Fuel Consumption[a]	Total Nickel[b]	ENVIRONMENTAL RELEASES				
			Air[c]			Land[d]	Water
			Total	< 3 µm	> 3 µm		
PRODUCTION							
Coal	617,600,000	8,300				---	6[d]
Bituminous	580,733,000	8,100					
Anthracite	949,000	47	neg[e]			neg[e]	
Lignite	34,354,000	100					
Petroleum	909,300,000	unknown					
Residual	154,600,000	7,700					
Distillate	754,082,000	neg					
ELECTRICITY GENERATION							
External Combustion							
Coal (total)	479,600,000	6,300	2,230	1,380	940	4,990	145[g]
Bituminous (total)	442,733,000	6,200	2,240	1,350	890	4,870	
Pulverized dry	336,477,000	4,700	1,740	1,030	710	3,670	
Pulverized wet	42,733,000	600	220	130	90	470	
Cyclone	53,128,000	740	240	180	60	560	
All stokers	8,855,000	120	40	10	30	170	
Anthracite (total)	949,000	47	15	5	10	40	
Pulverized dry	----						
Pulverized wet	----						
Cyclone	----						
All stokers	949,000	47	15	5	10	40	
Lignite (total)	34,354,000	100	30	24	10	80	
Pulverized dry	12,367,000	37	10	8	6	30	
Pulverized wet	2,405,000	7	3	2	1	5	
Cyclone	18,210,000	55	17	13	4	40	
All stokers	1,031,000	3	1	<1	<1	3	
Petroleum	77,850,000	3,620	3,620	3,480	140	140	
Residual oil	72,230,000	3,620	3,620	3,480	140	140	
Combustion turbine	83,600	4	4	4	<1	4	
Steam generation	71,910,000	3,600	3,600	3,460	140	140	
Combined cycle	328,600	16	16	15	1	1	
Distillate oil	5,582,000	neg[h]	neg[h]			neg[h]	neg
Combustion turbine	3,430,000	neg[h]	neg[h]			neg[h]	neg
Steam generation	1,484,000						
Combined cycle	667,500						
SPACE HEATING AND OTHER							
Coal[f]	138,000,000	1,930	620	190	430	1,740	neg
Industry	60,000,000	840	270	80	190	760	neg
Residential/Commercial	8,000,000	110	40	10	20	100	neg
Coke plants	70,000,000	980	310	100	220	880	neg
Petroleum	913,300,000	4,100	4,100	3,940	160	160	
Residual oil	82,400,000	4,100	4,100	3,940	160	160	
Industry	61,100,000	3,100	3,100	2,980	120	120	
Residential/Commercial	neg	neg	neg			neg	neg
Transportation	21,300,000	1,000	1,000	960	40	40	
Distillate oil	748,500,000	neg[h]	neg[h]			neg[h]	neg
Industry	80,000,000	neg[h]	neg[h]			neg[h]	neg
Residential/Commercial	189,000,000						
Transportation	479,500,000						

Table C-7. (concluded)

[a] Production and consumption data are from Monthly Energy Review published by National Reliability Council, Princeton, N.J. and are rounded to nearest thousand metric ton. Data may not add due to rounding.

[b] Nickel concentration by coal type is assumed to be: Bituminous coal - 14 mg/kg; Anthracite - 50 mg/kg; Lignite - 3 mg/kg (see Appendix B); also see Appendix A, note 7.

[c] The amount of nickel emitted to the atmosphere was calculated as follows:

$Q=(C)(F)$
Where Q=quantity of nickel in feed material
C=concentration of nickel in fuel, ppm
F=yearly consumption of fuel, metric tons per year

The amount emitted to the atmosphere, E, was
$E=(Q)(F)$

Where f is calculated in Appendix A; nickel associated with particles that are emitted to the atmosphere and are greater than 3μm in diameter settle out quickly and are thus included with land wastes (Lee and Duffield, 1979)

[d] The amount of nickel disposed to land was calculated as follows:

$L=(Q-E)+E_{>3\mu m}$
Where L=amount of nickel discharged to land;
Q=amount of nickel in fuel;
E=amount of nickel emitted to the atmosphere
$E_{>3\mu m}$=amount of nickel associated with particles greater than 3μm in diameter and that were initially emitted to the atmosphere, but eventually settled to land

[e] Nation emission burden from coal storage piles is estimated to be 630 kkg/yr; Blackwood and Wachter (1978). Nickel fugitive emissions are calculated using the following nickel concentrations: Bituminous coal - 14 mg/kg; Anthracite - 50 mg/kg; Lignite - 3 mg/kg.

[f] Acid mine drainage is reported to average 0.72 mg/l (range: 0.01 to 5.59 mg/l) at an average flow of 3.8×10^{6} liters per mine-day. Drainage from 5673 coal mines is considered in this calculation.

[g] Screening sampling data for the electric power operating point source category: the average flow from an ash pond is reported to be 21.7×10^{6} l/day-plant. Nickel concentration is reported to be 0.05 mg/l. Assuming each of the 379 steam electric plants identified to have an ash pond.

[h] See Appendix A, note 7, for details.

[i] Coal combustion exclusive of utilities is assumed to be in stoker fired boilers.

Table C-8. U.S. Fossil Fuel Consumption by User in 1979

USER	Coal (10^6 kkg)	%	Refined Petroleum Product (10^6 l)	%
Electric Utilities	480	78	83,315	8
Industry[a]	60	10	211,788	20
Coke Ovens	70	11		
Residential/Commercial	8	1	200,220	19
Transportation			564,132	53
TOTAL	618	100	1,059,894	100

Source: Monthly Energy Review, U.S. Department of Energy, 1980.

[a] Excluding coke ovens.

Table C-9. Sources of Nickel Contained in Sludge from Select Industrial Processes

PROCESS/WASTE	METAL PRODUCTION[a] 10^3 kkg	NICKEL CONCENTRATION OF WASTE, ppm	WASTE EMISSION FACTOR, kkg/kkg	DISPOSAL METHOD[b]	ENVIRONMENTAL RELEASES (kkg) LAND	WATER	AIR
Ferrous Metal Smelting and Refining							
Iron and steel coke production	90,938						
Iron and steel production	90,938						
Ammonia still lime sludge		10	0.00027	OD	0.25		52[c]
Basic oxygen furnace emission control sludge	55,472	65	0.0173	R, OD[d]	31		
Open hearth furnace emission control dust	17,278	240	0.0137	R, OD[d]	29		
Electric furnace emission control sludge	18,188	300	0.0087	R, OD[d]	24		
Rolling mill sludge	89,900	250	0.00174	OD	39		
			0.00016[e]	OD	6		
Cold rolling acid rinsewater neutralization sludge[e]	18,800	2000	0.0004[f]	OD	1.5		
Cold rolling mill waste H_2SO_4 pickle liquor	2,600	14	0.113	SL	41		
Cold rolling mill waste HCl pickle liquor		12	0.0536	OD	2		
Galvanizing mill H_2SO_4 rinsewater neutralization sludge	47,500	14	0.0108	OD	7		
Galvanizing mill HCl rinsewater neutralization sludge		12	0.0027	OD	2		
Decanter tank tar		10	0.0022	OD	2		
Ferrosilicon manufacture dusts	987[g]	3230	0.338	OD	1078		
Primary Nonferrous Smelting and Refining							
Copper smelting							
Acid plant blowdown sludge	1,340[g]	110	0.00270	TP	0.4		
Reverberatory furnace[d]							1
Electrolytic copper refining							
Mixed sludge	1,520[g]	10	0.0024[h]	OD	0.4		
Lead smelting							
Acid plant blowdown sludges	522,000[g]		0.040	SL, R	522		
Electrolytic antimony manufacture							
Spent anode sludge	13,700[g]	5	0.210	TP	14		
Secondary Nonferrous Refining							
Lead refining							
SO_2 scrubwater sludge	727,000[g]	5	0.045	SL (unlined)	164		
TOTAL					1958		53

Source: EPA 1978a.

[a] Based on product shipped unless otherwise noted; a blank means a negligible release.

[b] TP-Tailings pond; L-Landfill; R-Recycled; OD-Open dump; SL-Sludge lagoon; RS-Receiving stream

[c] See Appendix A, Note 4 for calculation.

[d] Assuming 50% of total wastes are recycled, EPA, 1978a.

[e] Cold rolling acid rinsewater neutralization sludge where acid is H_2SO_4.

[f] Cold rolling acid rinsewater neutralization sludge where acid is HCl.

[g] 1979 production data.

[h] Pickle bath may contain either HCl or H_2SO_4.

Table C-10. Nickel Wastes from Cement Plants in Metric Tons (kkg), 1979

Process	Cement Producted 10^3 kkg[a]	Emission Factor (kg/kkg)[b]	Total Particulates 10^3 kkg[c]	Environmental Releases (kkg)		
				Air[d]	Water[e]	Land[f]
Dry kilns	30,000	122	3,660	143	neg	1,872
Dryers, Grinders		48	1,440	56	neg	737
Total		70	5,100	199	neg	2,609
Wet kilns	41,600	114	4,700	182	neg	2,404
Dryers, Grinders		16	665	28	neg	340
Total		130	5,400	210	neg	2,762

---

[a] Total quantity of cement produced in 1979 was about 71.6 x 10^6 kkg; assuming 58% of production used wet method and 42% used the dry method (as was the case in 1976, Minerals Yearbook, 1976).

[b] Emission factors expressed as kg of particulate emitted without control devices per ton of cement produced (EPA, AP-42, Part B).

[c] The product of emission factor and cement produced.

[d] Assuming all cement plants have control devices; control device population equally distributed among multicyclones, electrostatic precipitators (ESPs), ESPs and multicyclones, and fabric filter units with 80, 95, 97.5, and 99.8% particulate removal efficiencies which when averaged equals 93%; number expressed is quantity of particulate matter emitted to atmosphere. Nickel concentrations in particulate matter emitted from cement plants after control devices range from 100-1,000 ppm (Lee and Duffield, 1979), and a mid-range value is used.

[e] Significant levels of nickel have not been detected in wastewaters from cement manufacture; i.e., mean values for nickel waste loadings were reported as zero, EPA, 1973c.

[f] Particulate matter removed by control devices with average efficiency of 93% (see footnote d).

Table C-11. Nickel Concentrations in Select Industrial Wastewaters

Industry	Firms Sampled	No. of Samples	Average Concentration mg/l
Meat Processing	16	53	0.07
Fat Rendering	4	16	0.028
Fish Processing	1	4	0.14
Bakery	3	8	0.43
Miscellaneous Foods	4	16	0.11
Brewery	2	43	0.04
Soft Drinks and Flavoring Syrups	3	12	0.22
Ice Cream	1	3	0.11
Textile Dyeing	22	65	0.25
Fur Dressing and Dyeing	6	28	0.74
Miscellaneous Chemicals	10	23	0.10
Laundry	4	14	0.10
Car Wash	39	39	0.19

Source: Klein *et al.*, 1975.

Table C-12. Nickel Content in Various Plants and Foodstuffs

Vegetable or Fruit	Concentration, ppm
	Wet Weight:
Potato, raw	0.56
Peas, fresh, frozen	0.30
Peas, canned	0.46
Peas, split, dried	1.66
Beans, string, frozen	0.65
Beans, string, canned	0.17
Beans, navy, dried	1.59
Beans, yellow-eye, dried	0.69
Beans, red kidney, dried	2.59
Spinach, fresh	0.35
Celery, fresh	0.37
Beet greens	1.94
Swiss chard, organic	0.71
Escarole, fresh	0.27
Chicory, fresh	0.55
Lettuce, garden, organic	1.14
Lettuce, head	0.14
Kale, organic	1.12
Kohlrabi, leavers, organic	0.47
Cabbage, white	0.14-0.32
Cabbage, red	0.24
Cauliflower leavers	0.19
Broccoli, fresh, frozen	0.33
Tomato, fresh	0.02
Tomato juice, canned	0.05
Apple, raw	N.D.[a]
Apple, raw	0.08
Banana	0.34
Pear	0.20
	Dry Weight:
Spinach	2.40
Squash	4.60
Tomato	0.01-0.154
Cabbage	3.30
Carrot, root	0.30
Carrot, leaves	1.80
Cress, water, tops	0.50
Cress, water, leaves	0.13
Mushroom	3.50
Peas	2.00-2.25
Potato	0.08-0.37
Onion	0.16
Lettuce	1.51
Lentils	1.61
Haricot beans	0.59
Orange	0.16
Apricot	0.64
Plum	0.90
Pear	0.90
Fig	1.20

Source: Nielsen, *et*, *al*., 1979.

[a] None detected.

Table C-13. Nickel Alloys: Percent Composition and Use

Components	%Ni	Alloy	Use/Properties
nickel	90-99.5	anodes	electroplating
nickel and iron	0.5-10	wrought alloy steels	transportation and earth-moving equipment; heavy machinery; low-temperature applications.
		wrought high-strength steels including maraging	hull plate; missile casings; machinery; forming dies.
	0.5-20	structural and high-strength cast alloy steels	heavy machinery; railroad; steel mill rolls; cryogenic applications.
	1-6 and 14-36	alloy cast steels	heavy machinery; machine tools; automotive and diesel engines; brake drums; corrosion resistance; abrasion resistance
	30-90	magnetic alloys	communications; electrical equipment.
	14-28	permanent magnet alloys and magnetic compensator alloys	motor, generator, radio, and instrument parts.
	4-90	nonmagnetic alloys	electrical and magnetic equipment parts.
	5-40	coated and clad metals	petroleum, chemical, and food-processing equipment
	22-50	thermal expansion and thermoelastic alloys	chronometer springs; electronic, instrument parts.

Table C-13. (Continued)

nickel and copper	2-13	high-copper alloys	instrument and control parts
	10-30	cupronickels	tubes and plates in condensers and heat exchangers
	25	coinage alloy	coinage
	over 50	high-nickel alloys	corrosion resistance; strength; chemical, petroleum, and food-processing equipment.
	5-30	nickel silvers (Ni-Cu-Zu)	flatware; hollow ware; electrical equipment telephone equipment; jewelry; zippers; plumbing fixtures; architectural trim
	1-15	nickel brasses and bronzes	spring applications; bearings; valves; pumps.
	45	electrical resistance alloy	resistance elements; thermocouples.
nickel and chromium (iron base and nickel base)	35-80	electrical resistance alloys	heating elements
	2-85	heat-resisting alloys	high-temperature applications
	10-80	superalloys	gas turbine and jet engine
	6-20	stainless steels	corrosion resistance; strength; chemical, petroleum, and food-processing equipment
others	0.5-98	age-hardenable alloys	corrosion resistance; strength
	98	composite	high-temperature applications
	94-98	nickel-manganese alloys	spark plugs; ignition tubes.

Table C-13. (Concluded)

	55-65	nickel-molybdenum-iron and nickel-molybdenum-chromium-iron alloys	corrosion resistance; strength
	85	nickel-silicon alloys	corrosion resistance; hardness alloys
nickel and aluminum	2	cylinder head and piston alloys	automotive and aircraft parts
	1-2.5	low-expansion alloys	automotive and aircraft parts
	1	bearing alloys	automotive and aircraft parts

Source: Adamec and Kihloren, 1968.

Table C-14. Composition of Nickel Plating Baths

TYPE OF BATH	COMPOSITION	CONCENTRATION (g/1)
Watts bath	$NiSO_4.6H_2O$	330
	$NiCl_2.6H_2O$	45
	H_3BO_3	38
Hard bath	$NiSO_4 6H_2O$	180
	NH_4Cl	25
	H_3BO_3	30
Chloride	$NiCl_2.6H_2O$	300
	H_3BO_3	38
Chloride sulfate	$NiSO_4.6H_2O$	200
	$NiCl_2.6H_2O$	175
	H_3BO_3	40
Sulfamate	$Ni(NH_2SO_3)_2$	450
	H_3BO_3	30
Sulfamate chloride	$Ni(NH_2SO_3)_2$	300
	$NiCl_2.6H_2O$	6
	H_3BO_3	30

Source: Lowenheim, 1979.

Table C-15. Wastewater Characteristics of Electroplating Shops

Plant	Flow Rate (gph)[a]	Nickel Content(mg/l)[b]	DISPOSAL Municipal	 Surface
A	800	0.6	X	
B	5000	1.0		X
C	3800	0.2	X	
D	11700	0.4	X	
E	3700	1.0	X	
F	8400	0.5		X
G	2100	1.7	X	
H	2500	1.9	X	
I	7500	2.0		X
J	3400	0.1	X	
K	44000	1.0		X
L	11500	1.4	X	
M	27000	2.0	X	
N	500	0.1	X	
O	360	2.7	X	
P	22300	4.7	X	
Q	41000	0.5	X	
R	3300	0.5		X
S	76800	0.4	X	
T	1900	3.0	X	
U	49200	0.1	X	
V	15000	0.8		X
W	13700	0.3	X	

Source: EPA, 1979b.

[a] Flowrates rounded to nearest 100 gallons per hour.
[b] Ni content rounded to nearest tenth.

Table C-16. Nickel Chemicals and Applications

Chemical	Application
Nickel Sulfate $NiSO_4$	Electroplating baths, fungicides
Nickel Chloride $NiCl_2$	Electroplating baths
Nickel Carbonyl $Ni(CO)_4$	Catalysis production of high purity nickel powder
Nickel Oxides NiO	Coloration of ceramics and glass, intermediate in production of other Ni chemicals
Nickel Cyanide $Ni(CN)_2$	Electroplating baths
Nickel Hydroxide $Ni(OH)_2$	Ni - Cd battery manufacture
Raney Nickel $NiAl_3$	Catalysis
Nickel Antimony Titanate	Production of paint pigments

Source: Antonsen and Springer, 1968.

Table C-17. Nickel in POTW Sludge: Selected Urban Cities

PLANT LOCATION	AVERAGE FLOW (10 l/day)	Ni concentration (µg/l) INFLUENT	EFFLUENT	SLUDGE
Indianapolis, IN	400	90	40	3343
Cincinnati, OH	30	30	20	3090
Lewiston, ME	38	62	42	478
Atlanta, GA	340	20	10	2567
St. Louis, MO	95	12	40	1070
Pottstown, PA	23	701	294	17000
Grand Rapids, MI	190	345	325	27300

Source: EPA, 1980b; 1980c.

Table C-18. Corrosion Rates of Nickel Alloys

Alloy (Ni%)	Conditions	Corrosion Rate (mpy)[a]
Hastelloy alloy B-2 (65)	99% acetic acid by wt[b]	0.3
	89% formic acid by wt	0.5
	70% sulfuric acid by wt	9.0
Inconel 600 (76)	50% phosphoric acid[c]	1.53
	35% hydrofluoric acid[d]	38.0
	60% sodium hydroxide[e]	4.0
Nickel 200 (99.5)	50% caustic soda[f]	1.1
	70% caustic potash[g]	0.4
Incoloy 825 (41.8)	10% oxalic acid[h]	20.0
	10% maleic acid[i]	0.1

Source: After Hughson, 1976

[a] Mil per year, 1 mil=0.001 inch.

[b] Boiling acids, laboratory tests of 120 hour duration.

[c] 30 day test.

[d] Acid temperature of 167° F.

[e] Boiling NaOH.

[f] Atmospheric pressure, 266° F, 720 hour test duration.

[g] Liquid velocity 21.6 ft/min., 300° F.

[h] 120 hour test.

[i] 120 hour test.

Table C-19. Name, Location, and Product Composition of $NiSO_4$-Containing Fungicides

```
*******************************************   **********************************   ********************************************
*REGISTRANT*       *NAME AND ADDRESS*

*  000550        VAN WATERS & ROGERS
                 AG. DEPT. (NAMCO)                            4082639900
                 2256 JUNCTION AVENUE
                 SAN JOSE, CALIFORNIA 95131

   *************** PRODUCT NAME ***************
                                                                                *APDATE*    *PM*    *DATE*    *TOXICITY*
   05579   GUARDSMAN NICKEL SULFATE
   *           *TYPE:  31  FUNGICIDE                                      OR    010176      21      0176         3
   *           *FORM:  15  SOLUBLE CONCENTRATE

                 *INGREDIENTS*
         050505  22.0000  Nickel sulfate hexahydrate

                                                                   **********  NUMBER OF PRODUCTS LISTED:       1
*REGISTRANT*       *NAME AND ADDRESS*

*  000707        ROHM & HAAS COMPANY
                 INDEPENDENCE MALL WEST
                 P.O. BOX 1348                                2155923000
                 PHILADELPHIA, PENNSYLVANIA 19105

   *************** PRODUCT NAME ***************
                                                                                *APDATE*    *PM*    *DATE*    *TOXICITY*
   00124   DITHANE S-31 AGRICULTURAL FUNGICIDE
   *           *TYPE:  31  FUNGICIDE                                            050175      21      0275         3
   *           *FORM:  03  DUST

                 *INGREDIENTS*
         014505  53.0000  Maneb ( manganese ethylenebisdithiocarbamate )
         050505  19.0000  Nickel sulfate hexahydrate

                                                                   **********  NUMBER OF PRODUCTS LISTED:       1
```

Table C-19. (Concluded)

```
*******************************************    ***********************************    *******************************************

  *REGISTRANT*      *NAME AND ADDRESS*

  *  000802      LILLY CHAS H COMPANY MILLER HD DIV
                                                          5032564600
                 7737 N.E. KILLINGSWORTH
                 PORTLAND, OR 97218

     **************** PRODUCT NAME ****************                                     *APDATE*    *PH*    *DATE*    *TOXICITY*

    00457   MILLER'S DITHANE S-31                                                        033171      21      0371          2
    *          *TYPE:  31  FUNGICIDE
    *          *FORM:  15  SOLUBLE CONCENTRATE

                    *INGREDIENTS*
             014505  53.0000  Maneb ( manganese ethylenebisdithiocarbamate )
             050505  19.0000  Nickel sulfate hexahydrate

                                                                               **********  NUMBER OF PRODUCTS LISTED:      1
*******************************************    ***********************************    *******************************************

  *REGISTRANT*      *NAME AND ADDRESS*

  *  011656      WESTERN FARM SERVICE, INC.
                 SHELL CHEMICAL COMPANY                   2022963633
                 1025 CONNECTICUT AVE, SUITE 200
                 WASH DC 20036

     **************** PRODUCT NAME ****************                                     *APDATE*    *PH*    *DATE*    *TOXICITY*

    05899   NICKEL SULPHATE                                                          OR    010176      21      0176          3
    *          *TYPE:  31  FUNGICIDE
    *          *FORM:  15  SOLUBLE CONCENTRATE

                    *INGREDIENTS*
             050505  22.0000  Nickel sulfate hexahydrate

                                                                               **********  NUMBER OF PRODUCTS LISTED:      1
```

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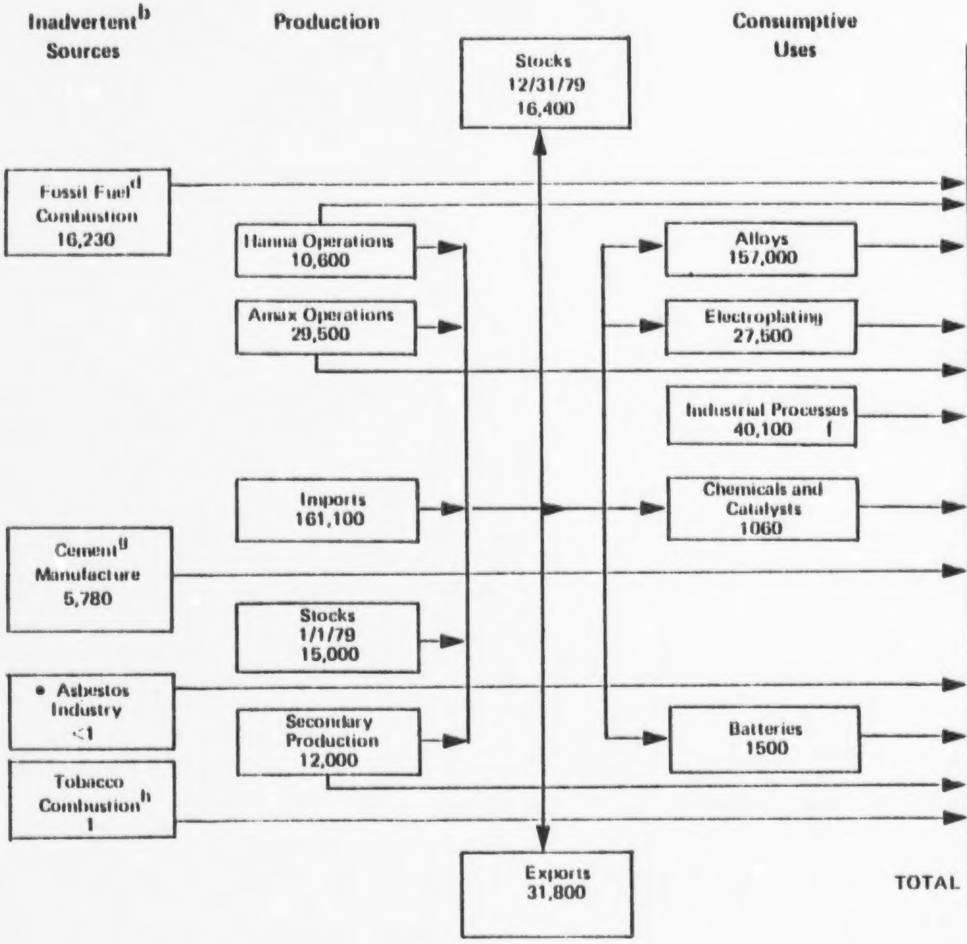
Table C-28. Metric Tons (kkg) of Nickel Released to Water from Selected Industrial Sources in Iron and Steel Manufacturing

	Waste Water Flow Rate (gal/ton product)[a]	TPD[b]	O/Y[c]	Concentration of Nickel after BPT (mg/l)[d,e]	Per Model Plant (kkg/yr)	Number of Plants with Process	Total Nickel Released to Water (kkg)[f] Surface	POTW
Ironmaking	125	6,000	365	0.15	0.15	54	7	
Sintering	100	4,000	365	0.35	0.19	11	5	
Hot Forming (pipe/tube carbon)	2,760	800	260	0.2	0.4	91	37	
Hot Forming (pipe/tube specialty)	2,760	770	260	0.2	0.4	21	8	
Scale Removal (Kolene specialty)	320	130	250	0.5	0.02	13		
Scale Removal (hydride)	100	200	270	0.5	0.01	8		
H_2SO_4 Pickling Batch (carbon--specialty)	600	500	260	0.2	0.06	116	3	
H_2SO_4 Pickling Continuous (carbon--specialty)	250	190	260	0.2	0.009	55		
HCl Pickling Batch (carbon--specialty)	705	190	260	0.2	0.026	7		
HCl Pickling Continuous (carbon--specialty)	130	2,760	312	0.2	0.2	91	14	6
Combined Pickling Batch (carbon--specialty)	540	200	260	0.2	0.02	70	2	
Combined Pickling Continuous (carbon--specialty)	1,540	500	320	0.2	0.19	74	14	
Cold Forming (cold roll recirculation, carbon--specialty)	25	1,700	340	0.2	0.01	170	2	
Cold Forming (cold roll combination, carbon--specialty)	250	4,400	347	0.2	0.29	20	6	
Cold Forming (cold roll direct application, carbon--specialty)	400	2,900	340	0.2	0.3	79	25	
Hot Coating (galvanized strip sheet and misc.)	600	800	260	0.5	0.24	44	7	3
Hot Coating (galvanized wire, wire products)	2,400	100	260	0.2	0.04	105	3	2
Hot Coating (terne, continuous strip sheet only)	600	165	260	0.4	0.039	6		
Hot Coating (other metalling coat, continuous/batch, strip sheet)	600	500	260	0.1	0.029	18	2	
Hot Coating (other metallic coating, continuous/batch wire)	2,400	15	260	0.1	0.01	18		
Hot Forming (primary carbon with scarfers)	1,700	4,430	260	0.2	1.48	91	119	7
Hot Forming (primary specialty without scarfers)	1,150	1,350	260	0.2	0.3	91	24	1
Hot Forming (primary specialty with scarfers)	1,700	1,350	260	0.2	0.45	21	9	
Hot Forming (section, specialty)	1,600	1,600	260	0.2	0.5	242	77	14
Hot Forming (flat/strip, carbon specialty)	4,400	8,300	260	0.2	7.1	56	309	20
Hot Forming (flat plate carbon)	2,300	4,050	260	0.2	2.27	25	52	5
Hot Forming (section carbon)	2,550	2,400	260	0.2	1.2	242	250	20
BOF (wet suppressed, carbon and specialty)	50	7,400	365	0.25	0.127	6		
BOF (wet open, carbon and specialty)	65	9,100	365	0.3	0.245	14	3	
Open Hearth (semi wet)	1,100	6,600	365	0.05	0.5	1		
Electric Arc (wet, carbon and specialty)	50	1,000	365	0.05	0.006	11		
Vacuum Degassing (carbon and specialty)	25	2,000	365	0.03	0.002	34		
				Total			1,066	90

[a] Model Plant data.
[b] Tons per day.
[c] Days of operation per year.
[d] Best Practical Control Technology.
[e] EPA, 1976.
[f] A blank space means < 1 kkg.
Source: EPA, 1980.


Inadvertent^{b} Sources
Production
Consumptive Uses
Stocks 12/31/79 16,400
Fossil Fuel^{d} Combustion 16,230
Hanna Operations 10,600
Amax Operations 29,500
Alloys 157,000
Electroplating 27,500
Industrial Processes 40,100 f
Imports 161,100
Chemicals and Catalysts 1060
Cement^{g} Manufacture 5,780
Stocks 1/1/79 15,000
• Asbestos Industry <1
Secondary Production 12,000
Batteries 1500
Tobacco Combustion^{h} 1
Exports 31,800

Environmental Releases (kkg)

	AIR	WATER^{c}			LAND	TOTAL
		(T)	(S)	POTW		
	8,990	150	150		7,030	16,170
	neg	1	1		2,600	2,600
	530	neg			neg	530
	neg	200	50	150	3,040	3,240
	30	132	132		132	295
	52	1,164	1,066	98	1,962	3,178
	neg	3	2	2	4	10
	409	neg^{i}			5,370	5,780
	1	neg	neg		neg	neg
	6	14	1	13	3	20
	9	688	411	275	570	1,270
	neg	neg			1	1
TOTAL	10,030	2,350	1,810	540	20,710	33,090

Note: Footnotes next page.

FIGURE C–1 ESTIMATED ENVIRONMENTAL RELEASES OF NICKEL IN 1979 FROM ITS INADVERTENT SOURCES, PRODUCTION, AND USE (kkg)^{a}

Figure C-1. (Concluded)

a) Total amount of nickel imported and produced minus that which is stockpiled and exported is equal to the sum of that used plus released; numbers do not add due to: rounding; unreported (confidential data) amount of nickel produced as by-product ($NiSO_4$) by select electrolytic copper refineries; and small quantities of nickel-containing materials may have been stockpiled from previous years by industries and are therefore not included in 1979 production figures; numbers from environmental releases correspond to those in Table 3-1. Table 3-1 should be referred to for further details.

b) Numbers reported as amount of nickel released from listed operations.

c) T=total, (S)+(POTW)=T, where S=surface waters and POTW=publicly owned treatment works.

d) Coal and/or petroleum products combusted by electrical utilities, industry, coke ovens, residential/commercial users and vehicles used for transportation.

e) Most coal-and oil-fired boilers released bottom ash and/or control device-collected flyash wastes to tailings ponds which were periodically dredged to land, Klein, et al., 1975.

f) Includes priamry and secondary ferrous and nonferrous smelting and refining; see Table 3-7.

g) Includes wet and dry processes, see Table 3-8.

h) See footnote Y, Table 3-1.

i) Significant levels of nickel have not been detected in wastewaters from cement manufacture, i.e., mean values for nickel waste loadings were reported as zero, EPA, 1973c.

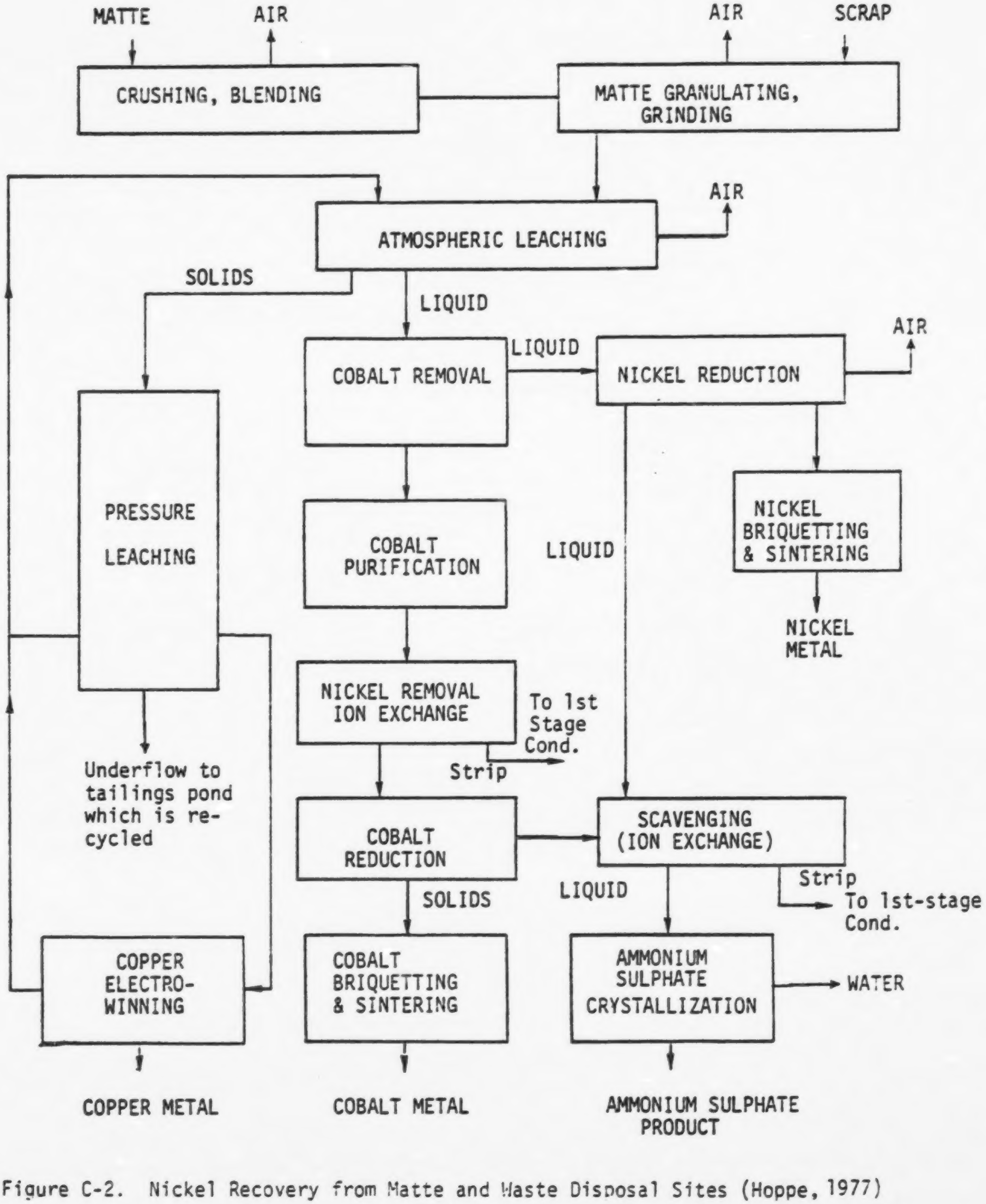

MATTE
AIR
AIR
SCRAP
CRUSHING, BLENDING
MATTE GRANULATING, GRINDING
AIR
ATMOSPHERIC LEACHING
SOLIDS
LIQUID
LIQUID
AIR
COBALT REMOVAL
NICKEL REDUCTION
PRESSURE LEACHING
COBALT PURIFICATION
LIQUID
NICKEL BRIQUETTING & SINTERING
NICKEL METAL
NICKEL REMOVAL ION EXCHANGE
To 1st Stage Cond.
Strip
Underflow to tailings pond which is recycled
COBALT REDUCTION
SCAVENGING (ION EXCHANGE)
SOLIDS
LIQUID
Strip
To 1st-stage Cond.
COPPER ELECTRO-WINNING
COBALT BRIQUETTING & SINTERING
AMMONIUM SULPHATE CRYSTALLIZATION
WATER
COPPER METAL
COBALT METAL
AMMONIUM SULPHATE PRODUCT

Figure C-2. Nickel Recovery from Matte and Waste Disposal Sites (Hoppe, 1977)

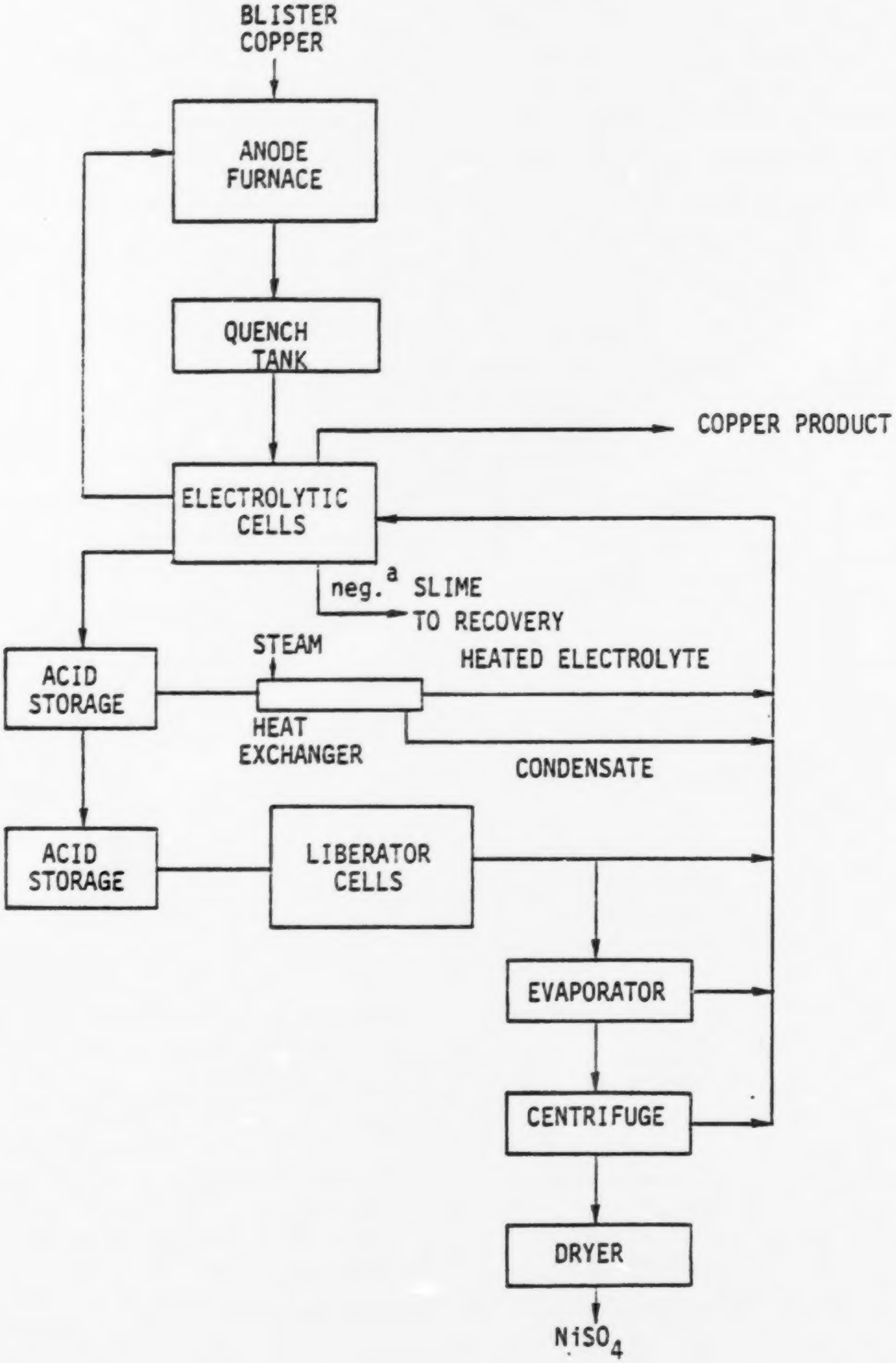

BLISTER COPPER
ANODE FURNACE
QUENCH TANK
COPPER PRODUCT
ELECTROLYTIC CELLS
neg.[a] SLIME TO RECOVERY
STEAM
HEATED ELECTROLYTE
ACID STORAGE
HEAT EXCHANGER
CONDENSATE
ACID STORAGE
LIBERATOR CELLS
EVAPORATOR
CENTRIFUGE
DRYER
NiSO4

Figure C-3. Generalized Flow Diagram of Electrolytic Copper Refinery (EPA, 1975a).

[a] Negligible to mean <1 kkg of nickel released per year.

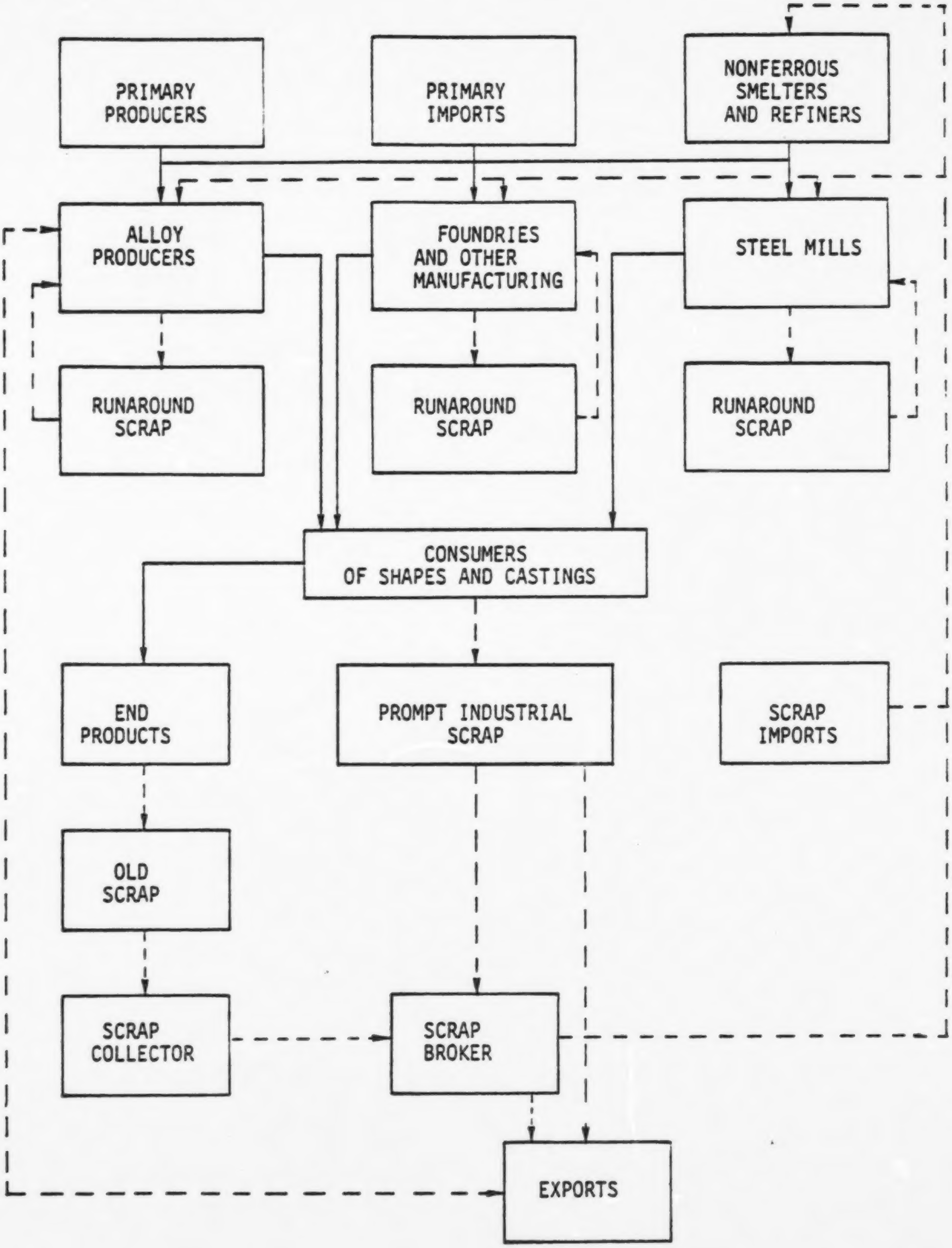

PRIMARY PRODUCERS
PRIMARY IMPORTS
NONFERROUS SMELTERS AND REFINERS
ALLOY PRODUCERS
FOUNDRIES AND OTHER MANUFACTURING
STEEL MILLS
RUNAROUND SCRAP
RUNAROUND SCRAP
RUNAROUND SCRAP
CONSUMERS OF SHAPES AND CASTINGS
END PRODUCTS
PROMPT INDUSTRIAL SCRAP
SCRAP IMPORTS
OLD SCRAP
SCRAP COLLECTOR
SCRAP BROKER
EXPORTS

Figure C-4. Market Flow Diagram of Old Nickel-Base Scrap (Matthews, 1979).

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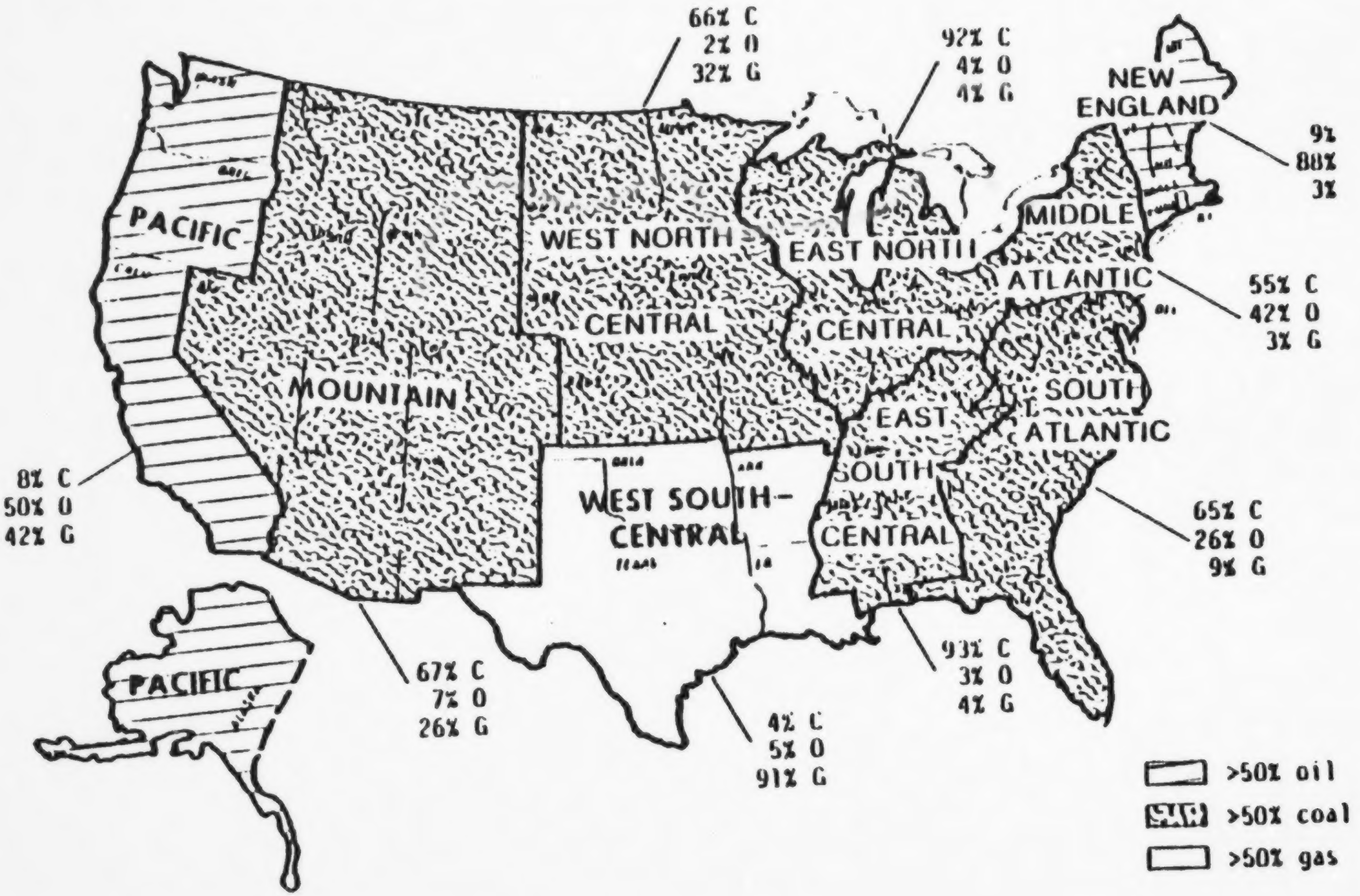

66% C
2% O
32% G
92% C
4% O
4% G
NEW ENGLAND
9%
88%
3%
PACIFIC
WEST NORTH CENTRAL
EAST NORTH CENTRAL
MIDDLE ATLANTIC
55% C
42% O
3% G
MOUNTAIN
EAST SOUTH CENTRAL
SOUTH ATLANTIC
8% C
50% O
42% G
WEST SOUTH-CENTRAL
65% C
26% O
9% G
PACIFIC
67% C
7% O
26% G
93% C
3% O
4% G
4% C
5% O
91% G
>50% oil
>50% coal
>50% gas

Figure C-5. Regional Fuel Distributions for Utility and Large Industrial Boilers

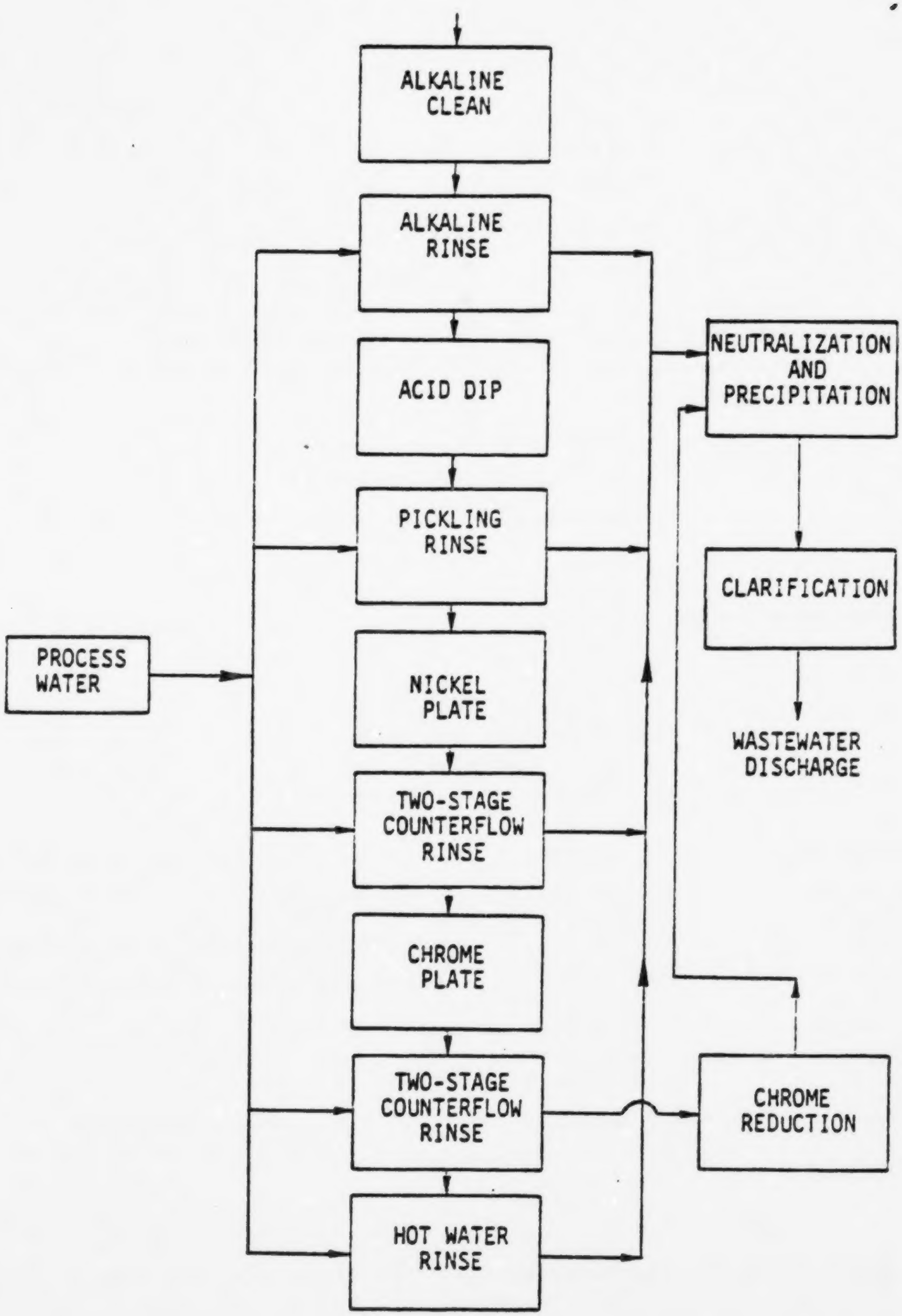
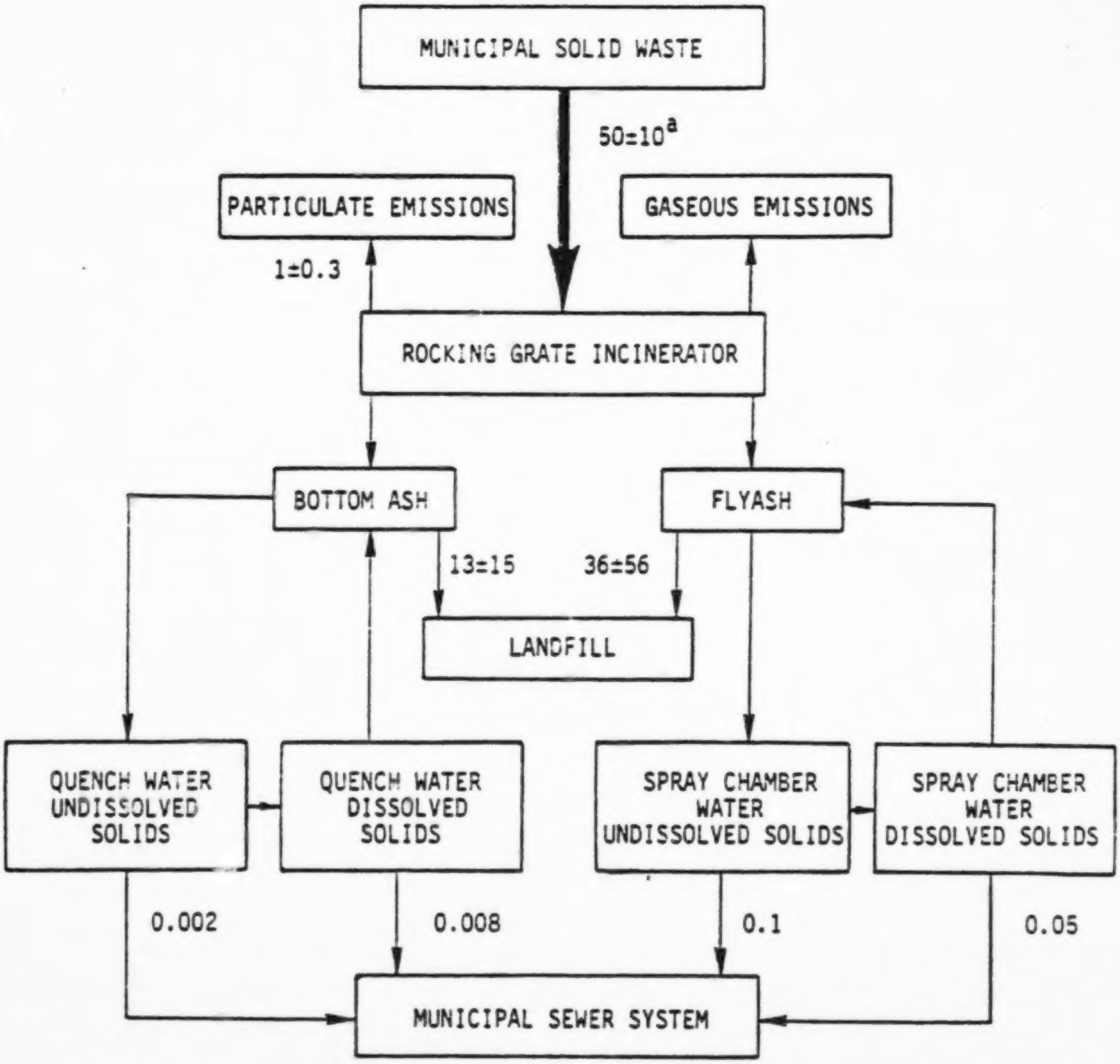

ALKALINE CLEAN
ALKALINE RINSE
ACID DIP
PICKLING RINSE
NICKEL PLATE
TWO-STAGE COUNTERFLOW RINSE
CHROME PLATE
TWO-STAGE COUNTERFLOW RINSE
HOT WATER RINSE
PROCESS WATER
NEUTRALIZATION AND PRECIPITATION
CLARIFICATION
WASTEWATER DISCHARGE
CHROME REDUCTION

Figure C-6. Nickel-Chrome Plate Sequence (Lowenheim, 1979).



MUNICIPAL SOLID WASTE
50±10[a]
PARTICULATE EMISSIONS
GASEOUS EMISSIONS
1±0.3
ROCKING GRATE INCINERATOR
BOTTOM ASH
FLYASH
13±15
36±56
LANDFILL
QUENCH WATER UNDISSOLVED SOLIDS
QUENCH WATER DISSOLVED SOLIDS
SPRAY CHAMBER WATER UNDISSOLVED SOLIDS
SPRAY CHAMBER WATER DISSOLVED SOLIDS
0.002
0.008
0.1
0.05
MUNICIPAL SEWER SYSTEM

Figure C-7. Flow Diagram of a Municipal Incinerator (Law and Gordon, 1979)[a]

[a] kg nickel per 920 kkg refuse/week.

APPENDIX D. CALCULATION OF RESPIRABLE NICKEL CONCENTRATION FROM A 1000-MW COAL-FIRED POWER PLANT

Table D-1 shows the assumptions used for the sample calculation.

The total amount of nickel emissions per year is assumed to be 1500 kg. This source strength is divided into three particle sizes as follows.

	Particle Size (μm)	Source Strength (%)	Source Strength (kg/s)
1.	0.5	25	1.20×10^{-5}
2.	3	60	2.85×10^{-5}
3.	10	15	7.00×10^{-6}

The settling velocity of particles is calculated using Stokes formula

$$V_s = \frac{d^2 g \rho_{ar}}{18 \mu_a} \qquad (1)$$

where d = diameter, m

ρ_{ar} = average density of particles, kg/m^3

μ_a = dynamic viscosity of air, kg/ms

g = acceleration due to gravity, m/s^2

The calculated velocities are as follows

$V_1 = 6.7 \times 10^{-5}$ m/s

$V_2 = 2.4 \times 10^{-3}$ m/s

$V_3 = 2.7 \times 10^{-2}$ m/s

The source depletion is calculated using the procedure described in Slade (1968). The source depletions in neutral atmosphere are shown for initial source heights of 100 m and 10 m, shown in Figure D-1. As can be seen from the figure, the depletion is negligible for particulates of diameter less than 3 m. Since nearly 85% of the source has a mean diameter less than 3 m, the respirable concentration of nickel resulting from coal-fired power plants can be very high.

The centerline ground level concentration is given by

$$C_i = \frac{\dot{Q}_x^{(i)}}{\pi \sigma_y \sigma_z \mu_w} \exp\left\{-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right\}$$

TABLE D-1. ASSUMPTIONS FOR SAMPLE CALCULATIONS OF NICKEL EMISSIONS IN THE ATMOSPHERE

Power Plant Capacity	1000 MW
Coal Used	Subbituminous
Type of Boiler	Tangentially fired with electrostatic precipitator[a]
Total Coal Consumption	2.6×10^6 kkg/yr
Total Fly Ash Generated	1.3×10^3 kkg/yr
Total Nickel Emissions	1500 kg/yr
Particulate Size	25% of 0.5 μm diameter
	60% of 3 μm diameter
	15% of 10 μm diameter
Stack Height	100 m
Atmospheric Stability	Neutral

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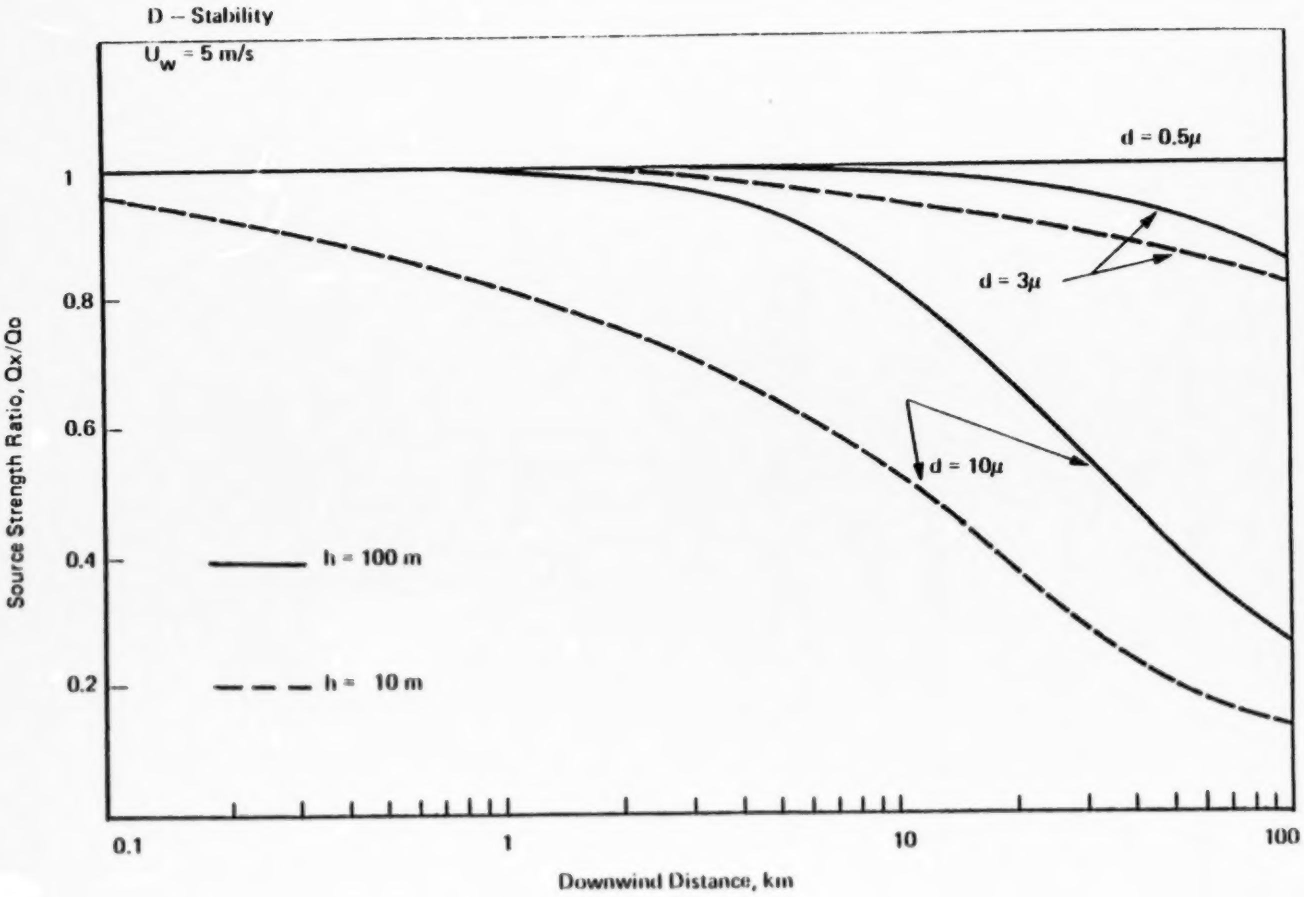
[a] This summary would not change significantly for different boilers with the exception of stoker boiler for which the emissions would be only slightly higher.

Source: Arthur D. Little, Inc.



Source: Arthur D. Little, Inc.

FIGURE D-1 SOURCE DEPLETION IN NEUTRAL STABILITY where $\dot{Q}_x^{(i)}$ is the depeleted source strength corresponding to a particle diameter d_i at distance x from the source. This can be obtained directly from Figure D-1. σ_y and σ_z are Pasquill-Gifford dispersion coefficients.

The total ambient centerline concentration is given by

$$C_{total}(x) = C_1 + C_2 + C_3$$

The total respirable concentration is given by

$$C_{res}(x) = C_1 + C_2$$

The total deposition rate is given by

$$w(x) = C_1V_1 + C_2V_2 + C_3V_3$$

Since V_1 and V_2 are very small, the predominant contribution to deposition comes from larger particles of greater settling velocities, V_3.

REFERENCE

Slade, D.H.; ed. Meteorology and atomic energy. Washington, DC: U.S. Atomic Energy Commission; 1968.

APPENDIX E. STORET RIVER BASIN CODES

This appendix contains listings of the major river basin codes which EPA has defined for the waterways within the United States. There are 23 major river basins defined within the United States. The listings are in order by major basin code.

A complete listing of these basin codes can also be obtained by listing the STORET help data set named BASIN.CODES.

Major River Basins

CODE	NAME
01	NORTHEAST
02	NORTH ATLANTIC
03	SOUTHEAST
04	TENNESSEE RIVER
05	OHIO RIVER
06	LAKE ERIE
07	UPPER MISSISSIPPI RIVER
08	LAKE MICHIGAN
09	MISSOURI RIVER
10	SOUTH CENTRAL LOWER MISSISSIPPI RIVER
11	COLORADO RIVER
12	WESTERN GULF
13	PACIFIC NORTHWEST
14	CALIFORNIA
15	GREAT BASIN
16	ALASKA
17	HAWAII
18	PUERTO RICO
19	VIRGIN ISLANDS
20	OCEANIA
21	LAKE HURON
22	LAKE SUPERIOR
23	HUDSON BAY